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Revegetation Strategies for Seawater Neutralized Bauxite Residue at Rio Tinto Alcan Using Various Amendments

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B.Sc

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Abstract

In northern Queensland, two alumina refineries process bauxite from a deposit which is located in far north Queensland. At both refineries the bauxite residue mud they produce is seawater-neutralized prior to its deposition in storage lagoons. This study was initiated to residue. There are, as yet, no published studies on the revegetation of such material although it is presumed, by some, that it will be less challenging than revegetation of non-neutralized residue (because it has a lower pH and ESP). Four experiments were carried out (two laboratory incubation studies, a greenhouse pot experiment and a leaching column experiment in the greenhouse).

In the first experiment, it was found that compared to non-neutralized bauxite residue from Western Australia (used in previous studies), seawater neutralized residue from north Queensland had a lower Si and quartz content but due to seawater neutralization it had a greater EC and exchangeable Ca, Mg, K and Na content and a lower pH (9.3 compared to 11.0-11.3) and ESP. Before revegetation, the accumulated salts would need to be leached out. However, during leaching the pH of both leachate and residue from north Queensland residue increased due to the dissolution of solid alkalinity while the opposite was the case for Western Australian residues.

In the second experiment, seawater neutralized bauxite residue was amended with residue sand (25% v/v), gypsum at 1% or 5%, poultry manure or biosolids (6% w/v) and incubated for 4 weeks and then leached with 6 pore volumes of water. After seawater neutralization the pH of unamended residue was 9.3 but during leaching it rose to 9.6. Addition of amendments had very small effects on physical properties of the residues while organic amendments increased the size and activity of the soil microbial community. After leaching, exchangeable Na, ESP and SAR were reduced by gypsum application and to a lesser extent by addition of poultry manure and biosolids. It was shown that even after seawater neutralization, exchangeable and soluble Na, ESP and SAR in residue were very high and applications of gypsum at about 5% and subsequent leaching would be required prior to revegetation.

In the third study greenhouse and laboratory experiments were carried out to evaluate the effects of addition of organic amendments, gypsum and subsequent leaching on improving the properties of residue as a growth medium for Rhodes grass and the effects of drying and rewetting on the physical properties of residue mud. In amended treatments, yields of Rhodes grass were greatly promoted by leaching (due to reductions in soluble Na, SAR and

EC) and were greatest in the leached biosolids plus gypsum treatment. It was also shown that when bauxite residue is dried, it loses considerable volume and forms a massive structure which when crushed, forms water-stable aggregates.

In the leaching column experiment, carried out over a 6-month period, all amendments were incorporated into the surface layer (0-10 cm). The main cation leached was Na^+ and the main balancing anions were Cl^- and SO_4^{2-}. During leaching, the pH of leachates rose from 7-8 up to 9-10 and concentrations of Al in leachates also rose. At the end of the study, gypsum plus organic amendments had the greatest effect in lowering exchangeable Na and pH in both the surface layer and the subsurface (10-30 cm) layers. Rhodes grass dry matter followed the order: control < gypsum < cattle manure < gypsum plus cattle manure < biosolids < gypsum plus cattle manure. When organic amendments were applied, root growth into the subsurface layer was greatly promoted.

It was concluded that although seawater neutralization of bauxite residue lowers the pH from 11-13 down to 9, subsequent leaching (which is necessary to leach out the excess salts accumulated during seawater neutralization) results in a rise in pH up to about 10 due to dissolution of residual alkalinity in the residue. Addition of 5% gypsum into the surface horizon can arrest this pH rise in that layer as well as promoting leaching of Na. To provide for a reduction in pH and more particularly a leaching of Na from both the topsoil and subsoil layers (with a reduction in exchangeable Na/ESP), a combination of gypsum plus organic amendments is highly effective. This allows root growth into the subsoil layers which is essential for plant survival during dry periods of the year. Prior to revegetation, the residue needs to be allowed to dry and solidify and the surface horizon can then be tilled to form a seed bed of water stable aggregates and fertilizers can then be added. In the future, field studies need to be initiated in north Queensland using such a strategy to field-test its effectiveness.

Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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Publications during candidature

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Incorporated as Chapter 3.

Contributor	Statement of contribution
Yaying Li	Designed experiments (70%) Wrote the paper (70%)
Richard Haynes	Designed experiments (30%) Wrote and edited paper (30%)
Ya-Feng Zhou	Assist of interpreting data and experimental instruction (100%)
Irena Chandrawana	Delivery of materials and industry support (100%)

Li, Y.[A], Haynes, R.[B], 2015. Chemical properties of seawater neutralized red mud in relation to revegetation. Proceedings of the sixth international contaminated site remediation conference. Crown Melbourne, Melbourne, Australia, 433-434.

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Contributor	Statement of contribution
Yaying Li	Designed experiments (70%) Wrote the paper (70%)
Richard Haynes	Designed experiments (30%) Wrote and edited paper (30%)

Contributions by others to the thesis

The most significant contribution made to this thesis (as previously listed) was by my principal advisor Professor Richard Haynes. My co-supervisor Dr. Ya-Feng Zhou was instrumental in the teaching of laboratory techniques and analytical assistance was provided by Katherine Raymont and David and Stephen Appleton.

Statement of parts of the thesis submitted to qualify for the award of another degree

None.

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Keywords

Bauxite residue mud, seawater neutralization, rehabilitation, revegetation, salinity, sodicity, organic waste, leaching, greenhouse study, column study.

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FoR code: 0502, Environmental science and management, 60%

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List of abbreviation

∑A	sum of anions
∑C	sum of cations
BS	biosolids
CEC	cation exchange capacity
c.f.	short for the Latin: *confer*, meaning “compare”
CM	cattle manure
$cmol_c$	centimoles of charge
C/N ratio	carbon/nitrogen ratio
$dS\ m^{-1}$	decisiemens per metre
DSP	desilication product
DTPA	diathylenetriamine pentaacetic acid
EC	electrical conductivity
ECEC	effective cation exchange capacity
e.g.	Short for the Latin: *exempli gratia*, meaning “for example”
ESP	exchangeable sodium percentage
G	gypsum
GI	germination index
ICP-AES	inductively couples plasma atomic emission spectroscopy
i.e.	Short for the Latin: *id est*, meaning “that is” or “in other words”
KPa	kilopascals
$mg\ m^{-3}$	megagrams per cubic meter
$mmol_c$	milimoles of charge
PM	poultry manure
µg	microgram
v/v	volume/volume
w/v	weight/volume
XRD	X-ray diffraction

1. General Introduction

Aluminium (Al) is the third most abundant element after oxygen and silicon in the lithosphere. It is widely used in packaging, transportation, building and construction and electrical goods. Reasons for its extensive use include its ready availability and desirable properties such as strength, good conductivity, light weight, malleability, ductility, corrosive resistance and easy recycling (Jones and Haynes, 2011). Aluminium occurs in the earth's crust mainly in mineral deposits (bauxite) which are rich in Al oxides such as gibbsite, boehmite and diaspore (Meyer, 2004). Bauxite is typically extracted by open cut mining from large blanket-type lateritic deposits. Following mining, the bauxite is crushed and then processed in an alumina refinery where the material is purified to produce Al oxide (alumina) which is then transported to an Al smelter.

The Bayer process is used in an alumina refinery whereby Al-containing minerals are digested in hot NaOH. The dissolved Al is then washed, dried and calcined prior to transportation to an Al smelter. Generally, 1-2 tonnes of bauxite processing residue are generated for every tonne of alumina produced (Power et al., 2011; Xue et al., 2016a). Bauxite residue has been produced since the development of the alumina industry in the late nineteenth century and it represents one of the largest volumes of industrial by-products produced by modern society. This residue is saline, sodic and alkaline due to the presence of residual NaOH (Grafe et al., 2011; Xue et al., 2016b). Globally, about 120 million tonnes of bauxite residue is produced annually and the global inventory reached more than 3.8 billion tonnes in 2016 (modified from Xue et al., 2016a). Although residues can be recycled to extract metals and produce construction and other types of materials, the volume recycled is less than 5% (Klauber et al., 2011). The bulk of the residues are transported to large storage areas which are typically adjacent to each alumina refinery. The stockpiling of residues and subsequent management of the storage areas represents a substantial cost to alumina production and is also a key environmental concern to the industry (Hausberg et al., 2000; Kumar et al., 2006). Environmental risks from these storage areas include wind and water erosion and drainage of leachate (Jones and Haynes, 2011; Power et al., 2011). For example, the alkaline, saline and sodic leachate may need to be managed and treated during operation of the refinery and then for many decades after closure. Several remediation measures have been employed to reduce the alkalinity of the residues prior to their deposition in storage areas including neutralization with CO_2, seawater and acid (Hanahan et al., 2004; Menzies et al., 2004; Khaitan et al., 2009; Sushil et al., 2012; Kirwan et al., 2013).

Australia is currently the world's largest producer of bauxite and in 2014, 81 million tonnes were produced (Statista, 2016). The Australian deposits are shallow and easy to mine by open cut

techniques. There are currently five bauxite mines in Australia providing feedstock for seven alumina refineries which in turn provide alumina to six aluminium smelters (Australian Aluminium Council, 2016). Each of the seven refineries have vast residue storage areas close-by. The five mines are Boddington, Huntly and Willowdale in Western Australia, Gove in the Northern Territory and Weipa in Queensland. While the Gove and Weipa deposits contain close to 50% available alumina and are amongst the world's highest grade deposits, the Western Australian deposits at Darling Range are considered as lower grade (about 30% available alumina) (Australian Aluminium Council, 2016).

In north Queensland, bauxite from far northern Queensland is processed at two alumina refineries. The residue is mainly mud (< 150 μm) with a small amount (about 3% of total mass) of sand (> 150 μm) present. Residues are seawater neutralized in especially designed facilities before deposition in the residue storage areas. Seawater neutralization was pioneered by the company and it results in the pH being reduced from 11-13 down to about 9.0 because soluble alkalinity is precipitated as poorly soluble Ca and Mg hydroxides and hydroxycarbonates (Hanahan et al., 2004; Palmer et al., 2009). Such neutralization not only alters pH but also reduces exchangeable Na percentage (by addition of Ca, Mg and K in the seawater) and it is also thought to influence the physical properties of the residues (Menzies et al., 2004; Hanahan et al., 2004).

Revegetation of bauxite residue storage areas is an extremely important issue for the alumina industry since it is a central component of the closure strategies for alumina refineries and it is required by most of the world's environmental regulatory agencies. Establishment of vegetation serves a variety of functions including stabilization of the residue surface against wind and water erosion, a reduction in leaching losses (due to water loss via evapotranspiration), provision of an aesthetically pleasing landscape and provision of a habitat for wildlife. Plant growth in residues is limited by alkalinity, salinity and sodicity (all caused primarily by the presence of residual NaOH in the residue), the lack of an adequate nutrient supply (due partly to the lack of organic matter and an active soil microbial community) and poor physical properties which are related to the very fine particle size of residue mud (Jones and Haynes, 2011; Grafe and Klauber, 2011; Xue et al., 2016a). In general, a period of years is required, prior to revegetation, in order to allow time for leaching of salts and alkalinity out of the surface layer of the profile. Tillage of the surface horizon, in order to improve physical conditions, and addition of amendments such as gypsum (to neutralize alkalinity and promote further leaching of Na), organic wastes (to improve nutrient supplying ability, improve physical conditions and promote soil microbial activity) and mineral fertilizers (to improve nutrient status) are also usually practiced prior to planting vegetation (Jones and Haynes, 2011; Xue et al., 2016a).

Previous CRC CARE/UQ research concentrated on the properties and revegetation strategies for bauxite residue sand originating from Western Australia (Jones et al., 2010, 2011, 2012a, b, 2015). This residue originates from a Western Australian bauxite deposit and because of its large quartz content it consists of about 30% residue sand. The sand is separated from the mud component prior to deposition in the storage areas and it is the sand component that is revegetated. The sand has a relatively low alkalinity and buffering capacity and is therefore easier to revegetate than the mud. This present study concentrates on the properties and revegetation prospects of seawater neutralized residue mud originating from an alumina refinery in north Queensland. While a large amount of research has concentrated on the properties and revegetation of bauxite residues very little work has been directed towards seawater neutralized residues. Indeed, although there are a few reports regarding the properties of such residues (e.g. Hanahan et al., 2004; Menzies et al., 2004, 2009; Palmer et al., 2009) to date no work has been reported on its revegetation.

The objectives of this study were to (i) compare the properties of residue mud and sand produced in Western Australia (as has been the focus of this CRC CARE/UQ laboratory over the last decade) with the properties of seawater-neutralized residue mud and sand produced in north Queensland (the focus of the present research), (ii) investigate the effects of amendment with residue sand, gypsum, poultry manure and biosolids and leaching on chemical, physical and microbial properties of mud, (iii) study effects of drying and rewetting on physical properties of mud and the effectiveness of leaching and additions of cattle manure, biosolids and gypsum in improving the properties of mud for growth of Rhodes grass and (iv) research effects of incorporation of amendments (gypsum and biosolids) into the surface horizon (0-10 cm) on the chemical composition of leachates, growth and chemical composition of Rhodes grass and the properties of the mud in a long-term (6-month) glasshouse column study. This thesis consists of a literature review on the nature of bauxite residues and the known effects of seawater neutralization (Chapter 2) followed by four research chapters (written as research papers) which investigate objective (i), (ii), (iii) and (iv)above. These are followed by a general discussion and conclusions section.

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2. Formation, properties and revegetation prospects for bauxite processing residue and the effects of seawater neutralization

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Abstract: For every tonne of alumina extracted from bauxite ore by the Bayer process (dissolution of Al-containing minerals in hot NaOH), 1-2 tonnes of alkaline, saline/sodic bauxite processing residue is produced. Partial neutralization of this residue prior to its deposition in land-based lagoons or impoundments minimizes the need to treat the alkaline, sodic drainage from the impoundments both during operation and following closure of the alumina refinery. For refineries close to the marine environment, seawater neutralization is a convenient technique. Some of the Na is replaced by Mg, Ca and K present in the seawater and reactive, soluble alkalinity is converted to poorly soluble alkaline solids (Mg and Ca hydroxides and hydroxycarbonates) with the result that the pH is reduced from 10-13 down to 8.5-9.5. Nevertheless, as yet, there are no reports of revegetation of the neutralized material. Growth limiting factors are likely to include alkalinity, sodicity, salinity, nutrient deficiencies and poor soil physical conditions. There are a number of questions related to revegetation of neutralized residue mud that need to be resolved including the extent to which the pH rises during storage (due to dissolution of residual solid phase alkalinity), the degree to which physical properties of mud are modified by neutralization (and agglomeration of mud particles), the severity of the key constraints to plant growth and therefore the potential need for addition of amendments (e.g. gypsum) and the role of added organic matter (e.g. biosolids, compost etc.) and soil fauna (e.g. earthworms) in improving physical conditions for plant growth. Future research needs to address these issues.

Keywords: bauxite residue, red mud, revegetation, Bayer process, seawater neutralization.

Biographical notes: Y. Li is an environmental science researcher working on revegetation strategies for bauxite residue mud. Her research pays particular attentions to the effects of seawater neutralization on the properties of residue mud and how this influences revegetation strategies.

R.J. Haynes is Professor of Soil and Environmental Sciences at the University of Queensland. He carries out research into revegetation strategies, constructed wetland technologies and waste management.

2.1 Introduction

The main source of aluminium is bauxite ore which contains gibbsite [$Al(OH)_3$], boehmite [γ-AlO(OH)] and/or diaspore [α-AlO(OH)]. The ore is typically excavated using open-cut mining techniques and then crushed and processed in an alumina refinery using the Bayer Process. This involves dissolving the Al-containing minerals in hot caustic soda (NaOH). The soluble product generates alumina, the precursor of aluminium, while the insoluble residue is separated and pumped out of the refinery as bauxite processing residue and deposited in land-based impoundments.

The engineered impoundments used for residue storage, often termed residue disposal areas (RDAs), typically occupy hundreds of hectares of land surrounding alumina refineries. Indeed, 1-2 tonnes of residues are generated per tonne of alumina produced (Hind et al., 1999; Kumar et al., 2006). On a global basis, bauxite residue production amounts to about 120 million tonnes per annum and the legacy of residue accumulation over the past 120 years is estimated to be approximately 3.8 billion tonnes in 2016 (modified from Power et al., 2011, Xue et al., 2016). Bauxite residues have a high pH (10-13) and possess high salinity and sodicity. As a result, drainage from the storage areas can pose an environmental risk and must be managed. Indeed, leachate from RDAs may need to be treated during operation of the refinery and then for many decades after closure. In addition, wind-blown alkaline dust from drying residue can pose a threat to wildlife and humans. As a result, some refineries now partially neutralize their residues before they are deposited in RDAs. This reduces the need for costly on-going intensive management of the RDA and its leachate after closure and also opens up opportunities for re-use of the residue which, to date, have been hindered because of the high pH (Kirwan et al., 2013).

Neutralization may involve (a) direct carbonation whereby the residue slurry is treated with CO_2 gas (Cooling, 2007; Dilmore et al., 2008), (b) addition of spent acids (Kirwan et al., 2013) or (c) reaction of residues with seawater (Hanahan et al., 2004; Palmer et al., 2009). Seawater neutralization was pioneered at the Queensland Alumina Limited refinery where, in order to conserve fresh water, seawater was used as a medium to transport residue from the refinery to disposal lagoons (Hanahan et al., 2004). An accidental consequence of this was partial neutralization. The pH is reduced by converting soluble reactive alkalinity to less soluble caustic solids such as calcite (Hanahan et al., 2004). Modern alumina refineries are often located close to deep water ports since this allows for

bulk shipment of incoming bauxite (sometimes from multiple sources) to the refinery and/or for bulk shipment of alumina to aluminium smelters situated elsewhere. There is therefore ample scope for the increasing use of seawater neutralization technology for pre-treatment of residues prior to their deposition in impoundments.

Revegetation of RDAs is a priority in closure strategies since it minimizes dust, reduces leaching (through transpiration losses to the atmosphere) and forms a landscape which is a habitat for wildlife. However, the saline/sodic nature of residues makes them difficult to revegetate (Grafe and Klauber, 2011; Jones and Haynes, 2011). Although a number of workers have characterized the seawater neutralization process (Hanahan et al., 2004; Menzies et al., 2004; Power et al., 2011), to date there are no reports on revegetation of this material. In this review we outline the processes of formation of bauxite processing residues, its key properties, alteration of properties induced by seawater neutralization and the prospects for its revegetation. It is not intended to provide an exhaustive review of papers on the subject but rather to highlight progress in the field, examine the mechanisms of formation and neutralization, identify limitations to revegetation and highlight areas where future research should concentrate.

2.2 The Bayer process and formation of bauxite residue

The Bayer process is the most widely used industrial method of producing alumina (Hind et al., 1999; Sidrak, 2001). It involves five major steps: grinding and pre-desilication, digestion, clarification, precipitation and calcination to alumina (Fig. 2.1). The bauxite is washed to remove residual materials, such as clays, and then crushed and ground to increase surface area. In many modern operations there is a pre-desilication step prior to digestion which removes reactive silica (predominantly present as kaolinite) that would otherwise cause scaling problems during digestion. This involves reacting the crushed material with hot NaOH to produce a slurry. Silicate minerals begin to dissolve in the liquor to form soluble sodium silicate:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6NaOH \leftrightarrow 2NaAlO_2 + 2Na_2SiO_3 + 5H_2O \quad (1)$$

The slurry is left in heated holding tanks for several hours to allow time for precipitation of desilication product (DSP):

$$6Na_2SiO_3 + 6NaAlO_2 + Na_2 + 12H_2O \overset{\Delta T}{\Leftrightarrow} 3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O)Na_2X + 12NaOH \quad (2)$$

The sodium aluminium silicate DSP mineral formed, $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O)Na_2X$ is sodalite where X^- can be a variety of anions, commonly CO_3^{2-}, OH^-, SO_4^{2-}. The structure of DSP is

discussed in more detail below. Slurry storage usually transforms 80-90% of the reactive silica into DSP, with the remainder being converted during digestion (Smith, 2008).

After desilication the bauxite undergoes digestion at elevated temperatures. The alumina phases are dissolved in the caustic solution to form sodium aluminate. Digestion conditions vary depending on the type of Al-containing minerals present in the bauxite. Diaspore and boehmite are less soluble in NaOH than gibbsite and therefore require greater energy inputs. Indeed, gibbsite can be digested in 3M NaOH with a temperature of only 100-150 °C but boehmites and diaspores require significantly higher temperatures and stronger NaOH concentrations (Lavalou et al., 1999; Authier-Martin et al., 2001; Mylona et al., 2008). The formation of sodium aluminate from bauxite minerals during Bayer digestion is as shown below:

$$Al(OH)_3(s) + NaOH(aq) \rightarrow Na^+Al(OH)_4^-(aq) \quad \text{(gibbsite)} \tag{3}$$

$$AlO(OH)(s) + NaOH(aq) + H_2O \rightarrow Na^+Al(OH)_4^- \quad \text{(boehmite and diaspore)} \tag{4}$$

Slaked lime [$Ca(OH)_2$] is often added to the liquor during digestion in order to remove impurities. These include carbonate, silicon, phosphorus and anatase and when lime is added sparingly soluble calcium carbonate, hydrogarnet, carbonate apatite and calcium titanate oxide are formed (Whittington and Fallow, 1997; Authier-Martin et al., 2001).

The next process is clarification in which the undigested bauxite residues are separated from the aluminate liquor and caustic soda is recovered. Firstly, via gravity, and sometimes cyclonic separators, the coarse particles (residue sand) are segregated. Secondly, in thickener vessels, synthetic flocculants such as polyacrylates, polyacrylamides are used for separating fine particles (residue mud) (Clifton et al., 2007; Pejcinovic et al., 2007). The mud, once separated, is washed using continuous countercurrent mud washers to recover liquor containing caustic soda and alumina.

In the precipitators, crystalline aluminium trioxide (gibbsite), which is termed hydrate, is precipitated from the digestion liquor:

$$Na^+Al(OH)_4^-(aq) \rightarrow Al(OH)_3(s) + NaOH(aq) \tag{5}$$

In order to induce precipitation, small crystals of trihydrate alumina are seeded into the cooled liquor. The finished mix of crystals is settled from the liquor stream and separated. The last phase is where the washed hydrate is calcined to form alumina. It is heated to 1000-1200 °C to drive off the water of hydration:

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g) \tag{6}$$

The final, white, sand-like product, alumina (Al_2O_3) is then transported to an aluminium smelter.

2.3 Bauxite processing residue

2.3.1 Storage/disposal

Throughout the world, the utilization of bauxite processing residue is very low (Paramguru et al., 2005; Klauber et al., 2011) so that the vast bulk of material is discarded in areas close to the alumina refinery. The stockpiling of residues in RDAs, and their subsequent management, represents a substantial cost in alumina production and it is also a key environmental concern for the industry (Hausberg et al., 2000; Kumar et al., 2006). At some refineries, the residue is separated into sand (>150 um) and mud (<150 um) particles and the sand is stored separately. These are usually refineries using low quality bauxite containing significant amounts of quartz. For most refineries using high quality bauxite deposits, sand particles make up a small proportion of the total residue (i.e. <5%) and they are not separated from the mud.

Marine discharge is the simplest method and involves residue slurry from the washing circuit being carried by pipeline well offshore for discharge into the deep ocean (Hausberg et al., 2000; Power et al., 2011). This was historically favoured by French and Japanese refineries. In 1965 about 30% of global alumina production was associated with such residue disposal but by 2011 this had been reduced to only 2-3% (Power et al., 2011). Due to increasing environmental awareness (Dauvin, 2010), increasingly strict environmental regulations, and international agreements with the International Maritime Organisation, the practice was discontinued by 2015.

The second residue management option is lagooning where the residue slurry from the washing circuit is pumped directly to land-based ponds. These are usually formed within natural depressions in the landscape and dams and other engineered earthworks are used to secure the residue containment. The alkaline liquid slurry can leach from lagoons and contaminate surface and/or groundwater (Cooling, 2007; Paramguru et al., 2005). Additional security can be achieved by using linings of compacted clay and/or synthetic membranes and the installation of engineered drainage networks (Hausberg et al., 2000). Storage problems can also be mitigated by partially neutralizing the slurry prior to discharge into the lagoon using seawater and/or mineral acids. The slurry in lagoons dries and consolidates over a long period and rehabilitation is only possible after this has occurred (Mahadevan and Ramachandran, 1996).

The current trend in residue storage is to move towards dry stacking (thickened tailings disposal) as the preferred technology. In this method, residue slurry from the washing circuit is thickened to a paste (48-55% solids) prior to discharge (Nguyen and Bodger, 1998; Cooling, 2007). The paste is transported by pipeline to the RDA where it is deposited on sloped beds (2-6°) in layers up to 0.5 m thick. The layer is then allowed to dry (by drainage and evaporation) to about 70% solids (Cooling and Glenister, 1992; Cooling, 2007). Evaporative loss is often promoted by turning the surface using earthmoving equipment. Once the bed has dried, the process is repeated by depositing a fresh layer of mud and the deposit is built up into a progressive stack. The process is designed so that the dried paste becomes self-supporting and as a result it can be safely stacked to considerable heights within containment embankments. Although dry stacking includes the additional step of thickening, it has many advantages over lagooning including minimization of (i) the size of the storage area, (ii) the structures needed for containment of the residue and (iii) the potential for leaching to groundwater and therefore contamination of ground and surface waters.

At the present time there is interest in mechanically removing as much water as possible from the residue (by a combination of thickening and filtration) to produce a dry cake with a solids content greater than 65%. The dry cake is transported to RDAs by conveyer belt or trucks. Such a strategy eliminates the need to remove liquids after deposition in the RDA and greatly reduces the potential for environmental impact especially contamination of surface and groundwater. Hyperbaric filtration of residue mud has been carried out successfully at a pilot scale (Bott et al., 2002) and dry cake disposal (following drying using vacuum drum filters) is already practiced at some refineries (Shah and Gararia, 1995). In situ compaction techniques can also be used once the residue has been deposited in the storage area. For example, Amphirol technology (use of screw-propelled vehicles) can be used to flatten and compact residues. By increasing surface area, amphirolling (mud farming) enhances evaporation and water loss from the deposted residue.

2.3.2 Properties of bauxite residues

Bauxite residues vary greatly in elemental composition depending primarily on the nature of the parent bauxite ore. Typical ranges of elemental content (as oxides) are: Fe_2O_3 30-60%, Al_2O_3 15-25%, SiO_2 1-20%, Na_2O 1-10%, CaO 5-40% and TiO_2 3-15% (Paramguru et al., 2005; Power et al., 2011). The material has a low organic C content (trace-0.3%) and is low in plant-available nutrients such as N, P, K, Ca, Mg, Cu and Zn (Jones and Haynes, 2011).

Concentrations of some heavy metals (e.g. Pb, Cd, Co, Cu, Zn, As) and naturally occurring radioactive materials (e.g. Th, U) are elevated compared to the parent bauxite due to their concentration in the waste stream during refining (Paramguru et al., 2005; Jones and Haynes, 2011). However, most metals are in non-mobile forms because of the high residue pH and radioactivity is typically extremely low (Von Philipsborn and Kuhnast, 1992; Qu and Lian, 2013).

2.3.3 Mineralogy

Bauxite residues typically consist of 70% crystalline mineral phases and 30% amorphous materials (Grafe et al., 2011). Mineralogical composition of residues depends on the nature of the bauxite ore used (since many minerals are carried over from the original bauxite) and the nature of new minerals created during the Bayer process. The major minerals in bauxite ores are gibbsite, boehmite, goethite, hematite, anatase, rutile, ilmenite, kaolinite and quartz (Bardossy and Aleva, 1990). Minerals commonly present in bauxite residues include the iron oxides hematite (Fe_2O_3) and goethite (α-FeOOH), Al oxides such as boehmite (γ-AlOOH) and gibbsite ($Al(OH)_3$), sodalite ($Na_4Al_3(SiO_4)_3Cl$), quartz (SiO_2), anatase and rutile (both TiO_2) and cancrinite ($Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$) (Table 2.1). Ilmenite ($FeTiO_3$), perovskite ($CaTiO_3$), tricalcium aluminate and hydrogarnet are other minerals commonly present (Grafe et al., 2011).

Because of the lower digestion temperature, the residues of gibbsitic bauxites have more minerals from parent ores than those from bauxites containing boehmite and diaspore. That is, under high temperature digestion, many of the major minerals are dissolved or react with other chemicals (Authier-Martin et al., 2001). Hematite is ubiquitous in residues and commonly has a concentration range of 7% to 29% (Grafe et al., 2011). Goethite occurs only when refining processes are at lower temperatures or the parent ores contain very large amounts of Al (Li, 1998; Li and Rutherford, 1996).

DSP (e.g. sodalite or cancrinite) are important components of bauxite residues because Na^+ and OH^- ions are slowly released from their mineral structure (Barrow, 1982; Wehr et al., 2006; Wong and Ho, 1995). Their structure is made up from SiO_4 and AlO_4 tetrahedra and they contain "cages" of negative charge (Fig. 2.2). Sodium ions balance this charge (Whittington et al., 1998; Smith, 2008). For chloride sodalite, the Na is present as $(Na_4Cl)^{3+}$ where Cl is tetrahedrally linked with four Na ions while for hydroxyl sodalite the Na is present as $(NaH_2O)^+$. Cancrinite has a different structure to sodalite and has two possible locations for included ions, either in the cage structures or in larger linear channels (Fig. 2.2) that form part of the hexagonal structure (Smith, 2008). Within these channels $2CaCO_3$ can replace Na_2X resulting in the formation of Ca cancrinite

[$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$]. This contains 25% less Na than sodalite. The Na^+ in sodalite and cancrinite cages can be replaced by other monovalent cations in the following order: $K^+ > Li^+ > NH_4^+$ (Wong and Ho, 1995) but divalent cations such as Ca^{2+} and Mg^{2+} are ineffective. Over time, Na is released from the DSP structure by sodalite/cancrinite dissolution and/or displacement by other monovalent ions.

Other DSPs include the tricalcium aluminate hexahydrate (TCA) ($CaO{\cdot}Al_2O_3{\cdot}6H_2O$) and the hydrogarnet series of minerals (Smith, 2008). TCA ($CaO{\cdot}Al_2O_3{\cdot}6H_2O$) is formed when lime is added to Bayer liquor. It is used as an aid to filtering during liquor clarification and it is also used as a desilication agent (Franca et al., 2010). For desilication, the TCA reacts with soluble silica to form a non-Na-containing DSP product, hydrogarnet [$Ca_3Al_2(SiO_4)_n(OH)_{12-4n}$] (Whittington and Fallow, 1997; Yuan and Zhang, 2009) thus minimizing the amount of soda lost with the residue mud.

2.3.4 pH and alkalinity

Residual NaOH is present in bauxite residues resulting in them being highly alkaline (Xue et al., 2016a). The pH of untreated residue liquor typically varies from 10.0 to 13.0 (Paramguru et al., 2005; Jones and Haynes, 2011; Grafe et al., 2011) and in the liquor the main alkaline anions buffering the solution are OH^-, CO_3^{2-}/HCO_3^- and $Al(OH)_4^-$. The alkaline buffering capacity of residues is maintained by alkaline solid phase minerals. These solids are formed during the Bayer process and the alkalinity originates from the NaOH and slaked lime ($CaOH_2$) present during digestion. As well as calcite ($CaCO_3$), sodalite, cancrinite, tri-calcium aluminate (TCA) and hydrogarnet are important buffering solids. For sodalite (Grafe et al., 2011), dissolution to form soluble alkalinity occurs as follows:

$$Na_6[Al_6Si_6O_{24}].2NaOH + 24H_2O = 8Na^+ + 8OH^- + 6Al(OH)_3 + 6\ H_4SiO_4 \quad (8)$$

Because of their alkalinity, bauxite residues have acid neutralizing capacity (ANC). This is measured as the amount of acid needed to reach a target pH. The ANC of bauxite residues (to pH 7.0) can range from 0.45 to 1.64 mol H^+ kg^{-1} (Snars et al., 2003, 2004) with an average of approximately 0.9 mol H^+ kg^{-1} (Grafe et al., 2011). There are several inflection points on ANC curves (Snars et al., 2004; Carter et al., 2008) reflecting the fact that, as noted above, there are a number of minerals contributing to the buffering capacity of residues (Khaitan et al., 2009). ANC values increase with increasing equilibration times up to several days (Liu et al., 2007; Carter et al., 2008) because neutralization reactions are limited by rates of dissolution of the solid phases. As noted by others (Xue et al., 2016a)

the behaviour and solubilisation of the insoluble alkalinity is poorly understood and requires further study.

For developing vegetation, the alkaline nature of bauxite residues is growth-limiting in a number of ways. In alkaline solutions, HCO_3^- predominates between pH 6.0 and 9.5 and CO_3^{2-} and OH^- above 9.5. Very high pH, with high concentrations of OH^-, CO_3^{2-} and HCO_3^- in solution, can impair root growth and function and nutrient translocation to leaves (Gupta and Abrol, 1990). The toxic effects of OH^- and HCO_3^- ions are similar in that they both cause inhibition of root growth (Kopittke and Menzies, 2004).

The high concentrations of aluminate [$Al(OH)_4^-$] present in solution at high pH (i.e. > pH 9.0) are also phytotoxic (Fuller and Richardson, 1986; Ma et al., 2003; Stass et al., 2006; Brautigan et al., 2012). The main mechanism of toxicity may be that aluminate forms a central core to Al_{13} species which are known to be highly phytotoxic (Kinraide, 1990; Kopittke et al., 2004a). Aluminium toxicity has been forwarded as a major limitation to plant growth in unamended bauxite residues by several workers (Fuller and Richardson, 1986; Courtney et al., 2009; Woodward et al., 2008).

2.3.5 Salinity

Electrical conductivity (EC) is measured to estimate total dissolved salt content and values for untreated bauxite residues range from 3,000 to 18,000 mS m^{-1} (Fuller et al., 1982; Snars et al., 2004). In a soil, values are typically less than 400 mS m^{-1} (Meecham and Bell, 1977a; Woodard et al., 2008) so that bauxite residues are considered as highly saline. Inhibition of plant growth (Maas, 1990) is usually slight at EC values between 200-400 mS m^{-1}, severe between 400-600 mS m^{-1} and death typically occurs at > 600 mS m^{-1} (Maas, 1990).

As a result of salinity, and a more negative water potential in soil solution, water uptake by plants is reduced (Keren, 2000; Yadev et al., 2011). The root-pressure-driven xylem transport of water and solutes is reduced as is shoot and root growth (Lauchli and Grattan, 2007; Yadav et al., 2011). Thus the salinity of freshly deposited bauxite residue will be a growth limiting factor for plants. However, over time the salts will be leached out of the surface horizons and down the residue profile. There is, nevertheless, the possibility that they may subsequently move back upwards in the profile by capillary action (particularly in residue mud deposits) (Wehr et al., 2006). Halophytic plants, tolerant to high salinity, are therefore appropriate for revegetation of bauxite residues (Bell et al., 1993; Jones and Haynes, 2011).

2.3.6 Sodicity

Exchangeable sodium percentage (ESP) and/or sodium adsorption ratio (SAR) are used to quantify sodicity (Sumner, 1995). The ESP is expressed as:

$$\mathrm{ESP} = \frac{100 \times \text{Exchangeable Na}}{\sum(\text{Exchangeable Ca+Mg+K+Na+Al})} \quad (9)$$

The SAR in soil solution, saturation paste extracts or soil/water extracts is defined as:

$$\mathrm{SAR} = \frac{\mathrm{mmol_c Na\ L^{-1}}}{\sqrt{\frac{(\mathrm{mmol_c Ca\ L^{-1}} + \mathrm{mmol_c Mg\ L^{-1}}}{2}}} \quad (10)$$

Soil sodicity is normally recognized when ESP values are > 15% or SAR values > 13 (Sumner, 1995). The ESP of bauxite residues is typically 60-90% (Meecham and Bell, 1977a; Fuller et al., 1982) so that it is sodic as well as highly saline.

Plant growth is inhibited by sodicity through a number of mechanisms. Excessive uptake and accumulation of Na leads to toxicity (Naidu and Rengasamy, 1993). Enzyme reactions can be inhibited by accumulation of Na in the cytoplasm while dehydration and death of leaf cells can occur where Na accumulates in the leaf apoplasm (Keren, 2000). In addition, high concentrations of Na in soil solution reduce Ca uptake and Ca deficiency often occurs (Kopittke and Menzies, 2005). A deficiency of Ca can influence membrane permeability and therefore restrict uptake of other ions resulting in deficiencies of N, K, Mn, Zn and Cu (Levy, 2000; Yadav et al., 2011).

2.3.7 Surface area and surface charge

The specific surface area of residue mud commonly ranges between 20 and 40 $m^2\ g^{-1}$ (Grafe et al., 2011). Such values are similar to those for 1:1 phyllosilicate clays such as kaolinite but are an order of magnitude less than those for expanding 2:1 clays such as the smectites. The net negative charge or cation exchange capacity (CEC) of residues has been reported to be 111-173 $mmol_c\ kg^{-1}$ by Meecham and Bell (1977a) and 42 $mmol_c\ kg^{-1}$ by Wong and Ho (1995).

The Fe and Al oxide materials in bauxite residues have variable charge surfaces so their net charge is dependent on factors such as pH and ionic strength. The pH where equal numbers of positive and negative surface charges exist (the point of zero charge) varies greatly depending on the nature of the parent bauxite and details of the Bayer process (Grafe et al., 2011). It has been reported to be 7.8-8.5 (Pradhan et al., 1999; Chevdov et al., 2001; Zhang et al., 2008), 6.9 (Lopez et al., 1998) and 6.0 or lower (Lopez et al., 1998; Castaldi et al., 2008). The variable charge nature of the Fe and Al oxide

surfaces means that residue can specifically adsorb both metal cations (e.g. Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}) and anions (e.g. phosphate, molybdate, asenate, vanadate) and because of this, and its substantial specific surface area, residue mud has been forwarded as a suitable material to remove such ions from wastewater streams (Paramguru et al., 2005; Wang et al., 2008).

The high adsorption capacity of residues means that micronutrient cations/heavy metal cations such as Cu, Zn, Mn, Pb and Cd as well as macronutrients such as P can be 'fixed' to the surfaces of the residue mud. For this reason, during revegetation fertilizer P applications are often large (see section 2.5.2). Adsorption of heavy metal cations is favoured by high pH so that leaching of heavy metals from RDAs is minimal but in some cases micronutrients such as Cu, Zn and Mn may be deficient and need to be added.

2.3.8 Physical properties

Since bauxite ores are crushed and then digested by the Bayer process, the particle size is mostly of a fine textural class, ranging from 100 nm to 200 µm with an average range of 2 to 100 µm (Pradhan et al., 1996; Roach et al., 2001). Soil particles are traditionally divided into size classes: sand (diameter 0.02-2.00 mm), silt (2 µm-0.02 mm) and clay (< 2 µm) and residue mud is typically in the silt and fine sand textural classes (Gee and Bauder, 1986). There are, however, large differences in size class between refineries. For example, Wehr et al. (2006) working at Gove, northern Australia, found that more than 50% of particles were clay-sized while Newson et al. (2006) reported most of the residues from a Scottish refinery were a mixture of sand and silt. Where the residue is lagooned, large particles settle first so that the material can become increasingly fine with increasing distance from the discharge point (Fuller et al., 1982).

The particle density of residue mud has been shown to range from 3.4-3.8 g cm^{-1} (Li and Rutherford, 1996; Li, 1998; Courtney et al., 2009). Residue mud can consolidate to form a solid mass and the bulk density is often in the range 1.5-1.8 g cm^{-1} (Nikraz et al., 2007; Courtney et al., 2009) and total porosity is about 0.53-0.63 cm^{-3} cm^{-3} (Wong and Ho, 1991, 1994a; Courtney et al., 2009). Because of the fine particle size, the pores present are all in the small size classes. A lack of macroporosity results in a low hydraulic conductivity (e.g. 0.002 cm min^{-1}) (Bell and Meecham, 1978). Residue sand (which is much coarser textured) has a lower water holding capacity than mud but a higher hydraulic conductivity (Wehr et al., 2005, 2006).

Because of the low macroporosity and hydraulic conductivity of mud, water tends to pond on the surface and the upper layers can become saturated during wet periods of the year. Such waterlogging

can limit plant establishment (Wehr et al., 2006) and installation of drainage to depth (i.e. several meters) is essential. In addition, a massive, solid, structure can develop in the surface horizons as a residue mud lagoon progressively dries. This limits both penetration and water infiltration (Newson et al., 2006; Harris, 2009). Such solidification develops due to the presence of binding agents in mud through the combined effects of silica, goethite, gibbsite and sodium silicate, amorphous goethite and hydrosodalite (Pinnock and Gordon, 1992; Zhang et al., 2001; Newson et al., 2006). Upon drying and solidification, the mud typically contracts and this can result in the formation of surface connected fissures and macropores to depth. In order to prepare the ground for revegetation, the profile may be deep ripped to a meter or more and then the surface layer (10-15 cm) tilled to form a seedbed using agricultural implements. This results in the formation of a mixture of size classes of solid peds and aggregates (bound together by the binding agents) and a physical environment which can be satisfactory for plant growth.

2.4 Seawater neutralization

2.4.1 Reaction mechanisms

Seawater typically contains 965 g of water and 35 g of salts (i.e. 3.5% salinity). The concentration of various salt ions in seawater is 55% Cl^-, 30.6% Na^+, 7.7% SO_4^{2-}, 3.65% Mg^{2+}, 1.17% Ca^{2+}, 1.13% K^+ and 0.7% other ions (Rai et al., 2013). For seawater neutralization, bauxite residues are mixed with seawater in a specialized facility and the neutralized residues are then rinsed with fresh seawater to remove entrained liquor. The process replaces some of the Na^+ with Ca^{2+}, Mg^{2+} and K^+ on exchange sites and soluble alkalinity is precipitated as sparingly soluble hydroxides and hydroxycarbonates (Hanahan et al., 2004). Neutralization is considered complete when the liquor from the treated residue mud has a pH less than 9.0 and a total alkalinity less than 200 mg L^{-1} (as $CaCO_3$ equivalent alkalinity) (Rai et al., 2012). Under field conditions the pH of seawater neutralized residues is typically in the range of 9.0-9.5.

The addition of seawater to residue mud results in the formation of fine mineral particles that flocculate into larger agglomerates (Palmer et al., 2009). Multivalent cations (Ca^{2+} and Mg^{2+}) originating from the seawater form electrostatic bridges and these act as nucleation sites for the precipitation of Ca and Mg hydroxides:

$$Mg^{2+} + 2(OH)^- \rightarrow Mg(OH)_2\,(s) \quad (11)$$

$$Ca^{2+} + 2(OH)^- \rightarrow Ca(OH)_2\,(s) \quad (12)$$

Formation of these solid phase hydroxides reduces the concentration of hydroxide in solution resulting in a decrease in pH. The decrease in pH also causes soluble aluminates to begin precipitating as AlO(OH) polymorphs and the concentration of extractable Al is decreased by seawater neutralization (Anderson et al., 2011). As electrostatic conditions on the surfaces change, the agglomerates tighten, pH decreases and elements that exhibited colloidal behaviour at high pH lose their stability. A further decrease in pH causes precipitation of hydroxycarbonates of aluminium, calcium, and magnesium, and precipitation of hydrotalcite-like compounds is favoured (Boclair and Braterman, 1999; Smith et al., 2005; Kirwan et al., 2013):

$$6Mg^{2+} + 8OH^- + 2Al(OH)_4^- + CO_3^{2-} \leftrightarrow Mg_5Al_2OH_{16} \cdot MgCO_3.4H_2O(\text{hydrotalcite}) \quad (13)$$

Hydrotalcite is a layered double hydroxide. Such compounds have the general formula: $[M(II)]_{1-z}[M(III)_z(OH)_2[A]_z.mH_2O$, where M(II) and M(III) are divalent and trivalent cations and A is an anion (e.g. CO_3^{2-}, SO_4^{2-}, OH^-, Cl^-, NO_3^-). Hydrotalcite is produced where M(II) = Mg^{2+}, M(III) = Al^{3+} and A = CO_3^{2-} giving the general formula $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. Layered double hydroxides consist of layers of metal cations M^{2+} and M^{3+} of similar radii which are randomly distributed in octahedral positions that form brucite-like structures (Fig. 2.3). The brucite-type layers are stacked on top of each other and held together by weak interactions. Substitution of divalent cations by trivalent ones gives rise to positively charged layers and in order to maintain neutrality, the interlayer region is occupied by an adequate number of anions, which are often hydrated (Fig. 2.3). Carbonate is the prevalent anion present during seawater neutralization and it is not readily exchanged with other anions. However, as pH declines during the neutralization process, there is a decrease in OH^- ions, (and therefore CO_3^{2-} ions), and intercalation of other anions is possible (Palmer et al., 2009).

It is important to note here that although the pH has decreased to 9.5 or below, no H^+ ions have been added to neutralize alkalinity. The alkalinity in the residue liquor has been neutralized by precipitation of sparingly soluble hydroxides and hydroxycarbonates. The alkalinity associated with the solid phase of the residue (Section 2.3.3) (i.e. sodalite, cancrinite, TCA and hydrogarnet), as well as the hydrotalcite, is still present so that over time, the pH of seawater-neutralized residue will tend to rise as these materials slowly dissolve. Menzies et al. (2009), for example, observed that during freshwater leaching of seawater neutralized residue sand, the pH of leachate rose from 8.0 to 10.1. They attributed this to a slow dissolution of sodalite.

2.4.2 Composition of neutralized residues

As expected the elemental and mineralogical composition of neutralized residues is similar to that of un-neutralized ones with hematite typically contributing about 60% of the mineral composition (Palmer et al., 2009). However, as already discussed, additional minerals are generated during neutralization. McConchie et al. (1999) noted that hydroxyl ions precipitated predominantly as brucite [$Mg_3(OH)_6$] but also as boehmite, gibbsite, hydrocalumite [$Ca_4Al_2(OH)_{12}\cdot CO_3$] hydrotalcite and p-aluminohydrocalcite [$CaAl_2(CO_3)_2(OH)_4\cdot 3H_20$]. During seawater neutralization Menzies et al. (2004) noted formation of a white precipitate which contained hydrotalcite, aragonite and pyroaurite. Hanahan et al. (2004) noted that the main additional minerals in seawater neutralized residue mud were hydrotalcite, hydrocalumite and p-aluminohydrocalcite.

2.4.3 Properties of neutralized residues

Depending on the solid to seawater ratio, neutralization proceeds through two or three buffering stages before reaching a pH of 8.2-9.0 (Hanahan et al., 2004; Menzies et al., 2004). Following seawater neutralization, residue surfaces have a greater Ca and Mg saturation although exchange sites are still dominated by Na (i.e. Na saturation is about 50%) (Hanahan et al., 2004). Thus, sodicity is decreased but there is an increase in salinity (EC) due to accumulation of cations in solution. These originate from those displaced from exchange sites plus those added in the seawater (Hanahan et al., 2004). The CEC remains essentially unaffected by neutralization (Hanahan et al., 2004; Menzies et al., 2004). Neutralized residues have an increased acid neutralization capacity due to the presence of large quantities of acid neutralizing hydroxycarbonate and hydroxyl-Al minerals (Hanahan et al., 2004; Palmer et al., 2009). The phosphate adsorption capacity of residues is increased after neutralization due to the anion adsorption capabilities of the precipitated hydrotalcides (Hanahan et al., 2004; Palmer et al., 2009). These materials remove oxyanions from solution through a combination of intercalation and adsorption onto external surfaces (Palmer et al., 2009).

Whether seawater neutralization significantly changes the physical properties of residue mud after deposition in the RDA is yet to be determined. Certainly, Rai et al. (2013) showed that in the laboratory, neutralized residue mud filtered twice as fast as un-neutralized mud and while the latter produced a reddish, turbid filtrate, that from neutralized mud was clear and devoid of colour. This was attributed to the fact that, as discussed previously, mud particles (< 5 um dia.) flocculate into larger agglomerates (80-400 um dia.) during seawater neutralization (Hanahan et al., 2004). Visual observations suggest that the seawater neutralized mud still tends to form a compact, solid mass within the RDA.

2.5 Revegetation

Since, as yet, there are no reports of revegetation of seawater neutralized bauxite residue, the appropriate amendments need to be deduced from the research literature on revegetation of un-neutralized residues plus the known physicochemical properties of the neutralized material. Apart from a lower pH, and the presence of some secondary minerals precipitated during neutralization, seawater neutralized residue has a very similar composition to un-neutralized residue. The same limitations to plant growth are therefore likely to be operative apart from, perhaps, severe alkalinity.

There are a number of alternative strategies for revegetation of bauxite residues. The conventional remediation technique was capping in which a cap of soil from 20-200 cm deep was placed over the RDA (Wehr et al., 2005, 2006). A shallow cap can support grasses and herbs whilst deeper caps may support trees and shrubs (Mendez and Maier, 2008). Often, a capillary break needs to be installed to prevent upward capillary rise of dissolved alkaline salts which then limits plant growth (Wehr et al., 2006). Because of the need for large amounts of soil and the fact that phytotoxic conditions in the residue below are not conducive to plant root growth, there is an increasing trend towards amending the residue and then seeding/planting directly into it.

Where the alumina refinery produces a substantial portion of residue sand, this can be separated and used to cap the residue mud (Eastham et al., 2006; Cooling, 2007). This means revegetation is into a less alkaline material with better physical properties than the mud. This technique is carried out successfully by Alcoa in West Australia as part of their dry stacking procedure (Cooling, 2007). Another option, where less residue sand is available, is to mix sand into the surface of the RDA to about 15 cm at a rate of about 25% (Courtney and Timpson, 2004, 2005; Courtney et al., 2009) thus improving physical conditions, at least in the surface horizon. The least desirable option is to revegetate directly into a well-drained residue mud profile. In any of the cases, other than capping with soil, the plants are seeded/planted into saline/sodic bauxite residue which normally needs additional amendments to make it a suitable growth medium. In addition, plant species need to be chosen carefully based on their tolerance to saline/sodic conditions.

2.5.1 Field neutralization

For un-neutralized residue, application of gypsum ($CaSO_4.2H_2O$) at 1-10% w/w is commonly practiced (Jones and Haynes, 2011; Xue et al., 2016b). The added Ca promotes precipitation of soluble alkalinity (HCO_3^-/CO_3^{2-}) as $CaCO_3$ resulting in a decrease in residue pH (Barrow, 1982; Jones et al., 2012a). Added Ca^{2+} also displaces Na^+ from exchange sites thus promoting leaching of Na^+

with the added SO_4^{2-} as a counterion. Even with added gypsum, the leaching of Na^+ out of the surface horizons can be slow and it can take months or even years before the medium is suitable for plant establishment and growth (Wong and Ho, 1993; Gherardi and Rengel, 2003). Following leaching, the ESP is typically reduced from 60-90% down to about 2-10% while pH is reduced from 10-12 down 8.0-9.0 (Wong and Ho, 1993, 1994b; Courtney et al., 2003; Ippolito et al., 2005; Xenidis et al., 2005). Since seawater neutralized residue typically has a pH around 8.5-9.5, it has been suggested by some that field neutralization will not be required. However, as already noted, seawater neutralized residues have an ESP of about 50% (Hanahan et al., 2004; Kopittke et al., 2004b) while values of above 15% are usually considered sodic and potentially plant growth-limiting. Thus, displacement of exchangeable Na^+ by added Ca^{2+} and other exchangeable bases (e.g. Mg^{2+} and K^+) would seem necessary.

In addition, field experience suggests that the pH of seawater neutralized residues tends to rise up to values of around 9.5-10.0 or above over the ensuing years after its deposition in an RDA. Indeed, a slow release of Na^+ and OH^- from residues is well documented due to the presence of DSP in bauxite residues (Barrow, 1982; Wehr et al., 2006; Wong and Ho, 1995; Menzies et al., 2009). As noted previously, Na^+ in the cage-like structure of sodalite is slowly released through slow dissolution of sodalite and/or displacement by other monovalent cations such as K^+. Other compounds which will contribute to residual alkalinity in residues include tricalcium aluminate and hydrogarnet. In addition, in seawater neutralized residues the newly precipitated Ca and Mg hydroxides and hydroxycarbonates represent another source of solid phase alkalinity that can potentially re-dissolve. Residual gypsum present in the residue may therefore be important since it will continue to dissolve releasing Ca^{2+} and SO_4^{2-} which helps neutralize this newly solubilized alkalinity as well as displacing released Na^+ and promoting its leaching.

Thus, it seems likely that gypsum applications will be beneficial for revegetation of seawater neutralized bauxite residue. In all probability, lower rates of application than those commonly used for un-neutralized residue will be sufficient since partial neutralization has already been achieved prior to deposition in the RDA. Added organic residues can have a similar neutralizing effect to gypsum (see below) so that where they are incorporated into surface layers, their effect may be sufficient to render gypsum applications unnecessary.

2.5.2 Nutrient additions

Fertilizer nutrient additions are required for revegetation because bauxite residues have a very low nutrient content. Rates used are generally high in the order of 250-270 kg N, 97-300 kg K, 200-300 kg P, 6-10 kg Ca, 30 kg Mg, 6-15 kg, Mn, 6-16 kg Mg, 0.2-0.25 kg Mo and 1.0-1.5 kg B ha^{-1} (Eastham and Morald, 2006; Meecham and Bell, 1977b). The application of P is typically high because of the high P fixation capacity of residue (due to its high content of Fe and Al oxides (Snars et al., 2004). Rates will need to be high in seawater neutralized mud since, as noted by Palmer et al. (2009), the neutralization process increases P fixation capacity.

The form of fertilizer nutrients applied may be important, particularly in the case of N. The high pH of bauxite residues favours NH_3 volatilization losses when NH_4^+-containing fertilizers are surface applied. In laboratory studies, Chen et al. (2010) measured very large losses of NH_3 (up to 95% of that added) when diammonium phosphate was applied to an un-neutralized residue sand (pH 11.6). The use of urea fertilizer should be avoided since when urea hydrolyses to form NH_4^+, the pH around granules is further elevated (Sommer et al., 2004). Ammonium may also accumulate in residues due to the lack of autotophic nitrifier bacteria (Meecham and Bell, 1977b) and high concentrations of NH_4^+ can be phytotoxic. Where ammonium-containing or forming fertilizers are used they need to be incorporated below the surface to avoid NH_3 volatilization losses. Fertilizer NO_3^- is an alternative that can be used. However, NO_3^- is highly mobile and could readily leach during periods of heavy rain. The use of controlled release fertilizers that release their nutrients (including NO_3^-) slowly over a period of months or years (Shaviv and Mikkelsen, 1993) is probably the most practicable solution during revegetation of residues.

Use of such slow release materials is an important consideration otherwise there will be a need to apply regular side-dressings. Indeed, after 5-10 years of revegetation, Courtney et al. (2009) observed nutrient deficiencies in plants growing in residue mud and stressed the importance of regular fertilizer applications. It would be desirable to practice regular soil and plant tissue analysis so that fertilizer nutrient rates could be altered based on the results obtained.

2.5.3 Organic matter additions

Organic matter performs many important functions in soils. These include (a) increasing water retention capacity, (b) forming a stable soil structure, (c) increasing cation exchange capacity, (d) supplying available nutrients (N, P, S) through mineralization and (d) providing a source of nutrients and energy for soil microorganisms and many soil fauna (Stevenson, 1994). Since the organic matter

content of bauxite residue is extremely low, additions of organic matter are likely to be extremely beneficial for revegetation (Xue et al., 2016b).

Thus, as expected, additions of manures, biosolids, composts and other organic wastes have been shown to greatly improve plant growth in bauxite residues (Fuller et al., 1982; Fuller and Richardson, 1986; Xenidis et al., 2005; Courtney et al., 2009; Jones et al., 2012a, b). The positive effects of these materials are at least partially due to increased macronutrient supply (N, P, K, Ca and Mg). Often there is also a decrease in pH, soluble and exchangeable Na and ESP (Wong and Ho, 1991, 1994b; Courtney at al., 2003, 2009). Acidification occurs because the organic materials normally have a lower pH than the residue and a high buffering capacity. The reductions in soluble and exchangeable Na and ESP are mainly attributable to additions of Ca, Mg and K in the manure which displace Na from exchange sites and this Na is subsequently leached. The increased CEC (and the additions of Ca, Mg and K) caused by organic matter additions also tends to lower the measured ESP (Jones et al., 2012a).

The addition of organic matter to the surface layers of bauxite residue will provide substrate for microbial activity. Indeed, bauxite residue is effectively a heat- and chemically-treated sterile inorganic material with an extremely low organic matter content. As a result soil microbial activity in the recently deposited material is low (Jones et al., 2010, 2011; Banning et al., 2011). Thus, the addition of organic manures, wastes and composts to bauxite residues causes a massive increase in the size and activity of the soil microbial biomass (Jones et al., 2010, 2011, 2012b). The microbial community (in association with soil fauna) carries out key functions including (a) synthesis and degradation of humic material, (b) mineralization of N, S and P, (c) formation and stabilization of soil aggregates. The development of a functioning below-ground ecosystem is essential for a sustainable above-ground ecosystem (Harris, 2003; Wardle and Peltzer, 2007) so that organic matter additions are a key consideration.

Organic matter additions also have extremely important effects on soil physical properties including increasing porosity and hydraulic conductivity and decreasing bulk density (Jones et al., 2010, 2011). In soils, linkage (with the aid of polyvalent cations) between mineral components (mainly secondary clay minerals) and humic material results in the formation of microaggregates (< 250 μm dia.) (Edwards and Bremner, 1967) and these are then linked together to form macroaggregates (> 250 μm dia.) by fungal hyphae, plant roots and other binding agents (Haynes and Beare, 1996; Bronick and Lal, 2005). Thus, addition of organic materials to residue mud is likely to initiate microaggregate formation through linkage of humified material to the Fe oxide surfaces of the residue mud. As noted above, flocculation of mud particles into larger agglomerates has been recorded during seawater

neutralization but how such processes would interact with organic matter-mineral particle-generated microaggregation has yet to be determined. Microbial activity, associated with the organic matter, along with root growth from planted vegetation is then likely to initiate macroaggregate formation. Thus, addition of organic matter to residues has been shown to increase macroporosity and stabilize structure (Wong and Ho, 1991; Jones et al., 2011). Large pores (macropores, > 30 μm) between macroaggregates can drain freely and are normally air-filled. They allow for gaseous exchange with the atmosphere, for percolation and drainage after heavy rainfall and growth of plant roots. Since the lack of macroporosity in fine-textured residue mud is a major constraint to plant growth, the effect of organic matter additions in generating aggregation is an important aspect that deserves future study.

Where solidification of residue mud is a problem, additions of organics (e.g. green manures) to the crushed surface mass can prevent re-solidification and create a more porous and stable topsoil structure (Harris and Rengasamy, 2004; Harris, 2009). In addition, an active soil microbial community helps in acidification of the residue. That is, CO_2 is produced by microbial respiration reacts with water to produce an acidic solution of carbonic acid which can then leach down the profile.

From the above discussion it is evident that there are a multitude of benefits from adding organic amendments other than nutrient supply. Thus, Bell et al. (2003) demonstrated that fertilizer alone was a poor substitute for organic amendments when rehabilitating bauxite residues. A combination of organic amendments and inorganic fertilizers is likely to give best results (Bell et al., 2003; Jones and Haynes, 2011).

2.5.4 Introduction of soil biota

Colonization of newly exposed parent material by soil microorganisms is rapid (Haynes, 2014). The major dispersal mechanism is aeolian transport of bacterial cells and fungal spores (e.g. in dust storms) although movement in water and by biological vectors can also be important. Microbial growth and activity is initially limited by low C and N availability so that during the initial stages of community assembly, heterotrophic microflora exist predominantly in resting stages. For example, Banning et al. (2011) found that bacterial and fungal communities developed rapidly on bauxite residues and diversity was similar to that under a coastal sand dune ecosystem after only 0.5 years of rehabilitation. Nevertheless, the size of the microbial biomass was very much smaller in the bauxite residue due to the low organic matter accumulation. The most practicable way of increasing microbial activity in residues is to add organic matter.

By contrast to microorganisms, colonization of new sites by soil fauna is more problematic and slower, particularly for non-winged organisms. Development of an active earthworm community, for

example, may take 30-50 years (Haynes, 2014). It has been suggested by a number of workers that inoculation with earthworms is an important strategy for mined land restoration (Snider and Hendrix, 2006; Butt, 2008; Boyer and Wratten, 2010) and earthworms have also been successfully introduced into mine tailings along with organic matter amendments (Cheng and Wong, 2008; Rutherford and Arocena, 2012). In the case of residue mud, introduction of earthworms along with organic amendments could have a range of beneficial effects, particularly on physical properties including macroporosity. For example, endogeic earthworms live in the top 15 cm of soil and ingest soil with a preference for particulate organic matter. They continually burrow and back-fill some of their burrows and other voids with their casts. They ingest organic residues, humified organic matter and mineral particles, mix them together and egest the mixture as casts. These casts have a higher microbial activity and nutrient content than surrounding soil and they can become stable macroaggregates (Tomlin et al., 1995; Laossi et al., 2010). In addition, their burrowing activity directly creates macroporosity in the surface horizon (Blanchard et al., 1999). In relation to physical properties, Marashi and Scullion (2004) showed that recolonisation with earthworms was a key factor in development of a macropore system in compacted soils formed after mining and that earthworm inoculation was an effective strategy.

Thus, introduction of earthworms to residue mud (along with organic amendments) could improve physical properties (particularly macroporosity) and plant growth and therefore be an important revegetation strategy. However, prior leaching to remove excess salts and reduce sodicity would be necessary since although the tolerance of earthworms to salinity/sodicity differs between species a high EC can bring about a cessation in reproduction (Owojori and Reinecke, 2009; Owojori et al., 2009) and even death (Guzte et al., 2011). Research on this aspect of revegetation is warranted.

2.5.5 Appropriate plant species

Selection of appropriate plant species is an extremely important aspect of successful revegetation. The species selected need to be able to tolerate high levels of salinity and sodicity and a high pH and most typically will come from maritime sand dune ecosystems or other systems where saline/sodic soils predominate. Mendez and Maier (2008) suggested successful revegetation of mine tailings involves biomass production comparable to uncontaminated soil, self-propagation, establishment of native colonizers, long-term survival and accumulation of only trace amounts of heavy metals in shoots. The long-term aspect of revegetation of bauxite residues (e.g. > 10 years) is not well studied since most workers have concentrated on the establishment phase (Wehr et al., 2006; Courtney et al., 2009). More long-term experiments are required.

In the field study of Courtney et al. (2009) residue was seeded with four grass species and two legumes but after 6-9 years, 47 species belonging to 38 genera and 15 families were present. *Holcus lanatus*, *Fescue rubra*, *Agrostis stolonifera*, which were seeded, were the dominant grass species. As well as the originally seeded legumes (*Trifolium repens*, *T. pratense*) several others were also present including *Lathyrus pratensis*, *Lotus corniculatus*, *Medicago lupulina* and *Vicia sepium*. Since legumes have the ability to fix atmospheric N_2 symbiotically, they have an advantage where the soil N supply is poor. Courtney et al. (2009) noted that in general, the dominant species that invade residues are those that have high seed production rates, are easily dispersed and have tolerance to both local climate and the potentially damaging soil conditions. Other herbaceous species that have been successfully grown on residues include salt tolerant grasses such as Rhodes grass (*Chloris gayana*), Yorkshire Fog, (*Holcus lanatus*), perennial ryegrass, (*Lolium perenne*) and Wimmera ryegrass, *Lolium rigidum* (Meecham and Bell, 1977b; Bell et al., 1989; Courtney and Timpson, 2004; Eastham et al., 2006) as well as pasture legumes such as red clover *Trifolium pratense* (Courtney and Timpson, 2005; Courtney et al., 2003).

In many situations it may be desirable to revegetate with plants from a native woody shrub ecosystem so that the RDA blends back into its natural environment. Bell et al. (1993) screened 29 native Australian woody plants which grow naturally in saline conditions and found survival and growth in bauxite residue under field conditions was predicted by their short-term response under glasshouse conditions. Species which survived well included *Melaleuca nesophila, Tamarix aphylla, Eucalyptus loxophleba*, *Acacia saligna*, *E. gracilis*, *E. Conferruminata*, *E. tetragona* and *E. platypus*.

2.6 Synthesis and Conclusions

2.6.1 General considerations

Bauxite residue is an alkaline, saline/sodic material that is stored in large engineered lagoons and impoundments surrounding alumina refineries. The material represents an environmental risk since drainage may contaminate surrounding surface and groundwater and alkaline dust can present a risk to plants and animals. Closure of these areas will normally involve revegetation and the continuing expense of ongoing management of the impoundment and treatment of drainage. There are both chemical (salinity, sodicity and alkalinity) and physical (fine texture, low hydraulic conductivity, poor drainage) constraints to revegetation of residue mud. While alleviation of soil chemical properties through addition of gypsum and leaching is well documented, amelioration of physical constraints is much less well understood. An important strategy could well be addition of organic

matter (biosolids, composts etc.) and earthworms to the surface horizon resulting in formation of macroaggregates and and macroporosity. This would involve:

- Linkage of organic matter molecules to the Fe oxide surfaces on residue mud resulting in the formation of microaggregates
- Microbial activity (associated with the added organic matter) and plant root growth then generating macroaggregation
- Development of macropores within inter-aggregate spaces between macroaggregates
- Introduction of soil fauna (e.g. earthworms) which would generate further macroaggregation (through intimate mixing of organic and mineral components) and formation of macroporosity (through burrowing)

Further research is needed on the above topics because establishment and plant growth on residue mud is greatly restricted by physical constraints. Research is required to investigate these aspects since physical constraints to the establishment and growth of plants in residue mud are considerable.

2.6.2 Seawater neutralized residue

Because treatment of drainage from RDAs will be an ongoing requirement after closure there is an increasing trend towards partial neutralization of residues before they are deposited in storage areas. Several refineries close to the sea have already installed dedicated seawater neutralization plants and with the trend towards locating refineries close to deep water ports, there is scope for greatly increased use of this technology. By the addition of Ca and Mg from the seawater, alkaline buffering anions in the residue liquor are neutralized by precipitation of poorly soluble hydroxides (calcite and magnesite) and hydroxycarbonates (e.g. hydrotalcite). As a result, pH is reduced from 10-13 down to about 8.5-9.5.

To date, there are no reports on revegetation of seawater neutralized residue mud. Nevertheless, revegetation is an important component of closure strategies since it not only improves the aesthetic setting and minimizes dust but the growing plants continually remove water via transpiration thus reducing drainage. Plant growth-limiting factors are likely to be similar, but less intense, to those for un-neutralized residues and include salinity, sodicity, alkalinity, deficiencies of macro- and micronutrients, lack of macroporosity and consequent waterlogging and solidification.

There are a number of unanswered questions that require future investigation related to the management of RDAs containing seawater neutralized residues. These include:

- To what extent does the initial pH of 8.5-9.5 rise during storage as a result of the presence of a buffering reserve of alkalinity? Unpublished observations have indicated a measurable rise to above 9.5.
- How does an increase in pH with time effect properties of the residue (e.g. alkalinity, sodicity, soluble Al content)?
- Does agglomeration of residue mud particles during seawater neutralization substantially alter the physical properties of mud after its deposition in the RDA?
- What are the key limiting factors to revegetation in the short and longer-term? To what extent does seawater neutralization require revegetation strategies developed for non-neutralized residues to be modified and/or changed?
- What are the most effective ameliorative amendments (organic wastes, gypsum, fertilizers) and how should they be applied and managed?

With large volumes of seawater neutralized residues now being produced, and prospects for much greater volumes in the future, it is important that these questions are answered promptly.

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Table 2.1 *Mineralogical composition of bauxite residues from various regions of the world.*

Country	Region	Hematite	Goethite	Boehmite	Gibbsite	Calcite	Quartz	Rutile	Anatase	Sodalite	Cancrinite	Reference
Australia	Weipa	●	-	●	●	●	●	-	●	-	●	(Palmer and Frost, 2008)
Australia	Kwinana	●	●	●	●	●	●	-	●	●	-	(Jones et al., 2010)
India	East coast	●	●	●	●	●	-	●	●	●	●	(Rai et al., 2012)
Italy	Sardinia	●	-	●	●	-	●	-	●	-	●	(Garau et al., 2007)
Brazil	Sao Paulo	●	●	-	●	-	●	-	-	●	-	(de Souza et al., 2013)
Brazil	Southern area	●	●	-	●	-	-	-	●	●	-	(Li and Rutherford, 1996)
Ireland	Aughinish	●	●	●	●	●	●	●	-	●	-	(Atasoy, 2007)
Turkey	Seydishir	●	●	●	●	●	-	-	-	●	-	(Atasoy, 2007)
Jamaica	Arvida	●	●	●	●	●	-	-	●	●	-	(Ludwig, 1987)

● detected
- not found

Figure Captions

Fig. 2.1 A schematic diagram of the Bayer process.

Fig. 2.2 A structural model of negative charged cages and linear channels of cancrinite and sodalite. Redrawn from Zhao et al. (2004).

Fig. 2.3 A schematic representation of hydrotalcite structure. Redrawn from Palmer et al. (2009).

Fig. 2.1

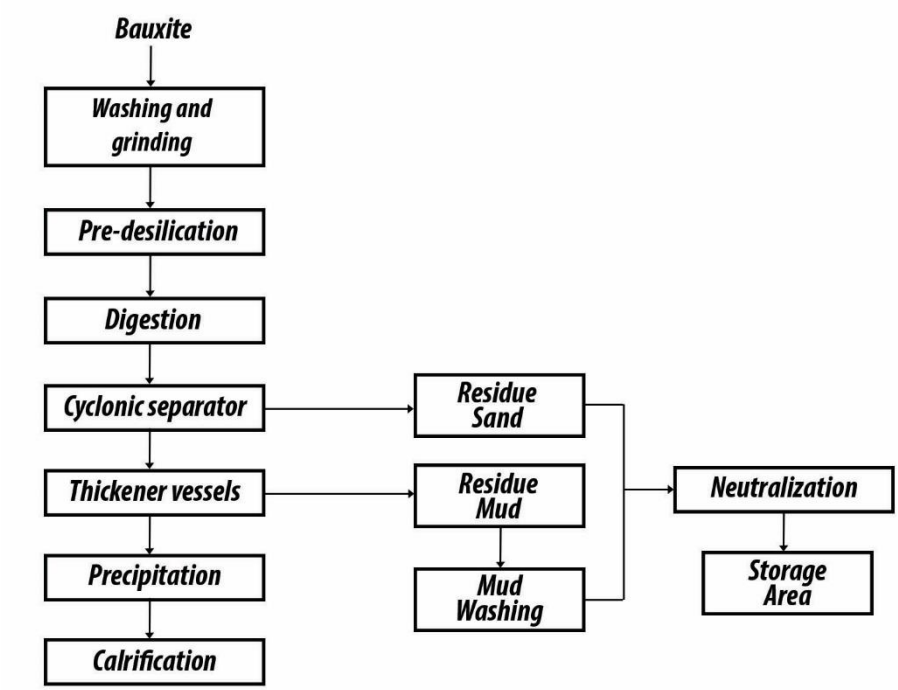

Bauxite
Washing and grinding
Pre-desilication
Digestion
Cyclonic separator
Thickener vessels
Precipitation
Calrification
Residue Sand
Residue Mud
Mud Washing
Neutralization
Storage Area

Fig. 2.2

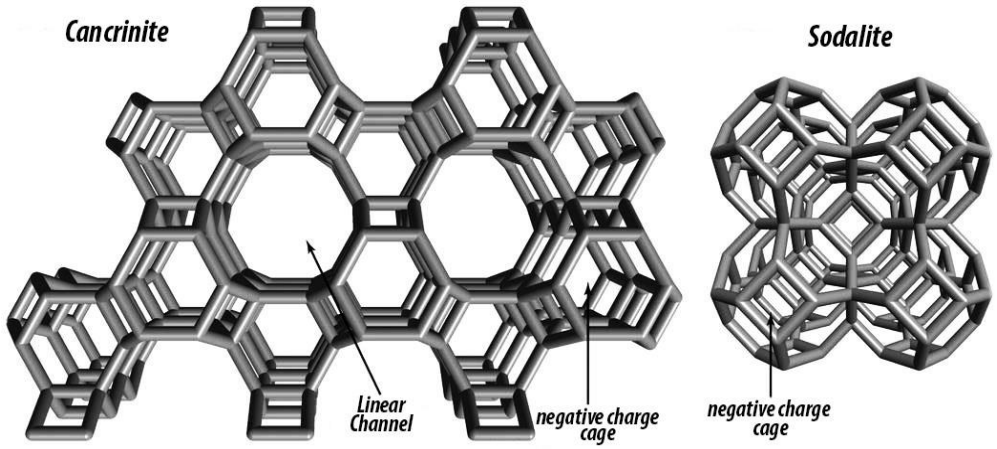
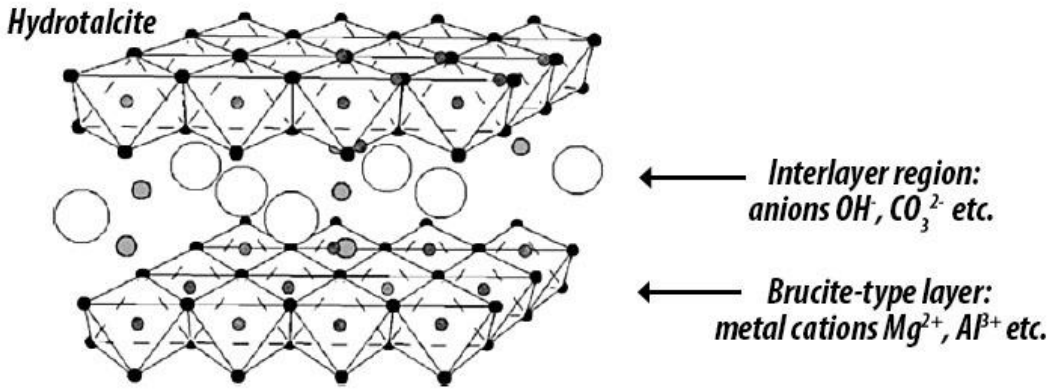

Cancrinite
Linear Channel
negative charge cage
Sodalite
negative charge cage

Fig. 2.3


Hydrotalcite
Interlayer region:
anions OH^-, CO_3^{2-} etc.
Brucite-type layer:
metal cations Mg^{2+}, Al^{3+} etc.

(Due to commercial considerations this chapter was submitted for publication as two separate papers; see appendices 1 and 2)

3. Physical and chemical properties of bauxite residue mud and sand from two different sources and pre-treatments and the effects of leaching

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Abstract: Bauxite processing residues (mud and sand) originating from the two main sources of bauxite that are currently being mined and processed for alumina production in Australia (north Queensland and Western Australia) were collected and characterized. Mixtures consisting of 0:100, 25:75, 50:50, 75:25 and 100:0% v/v residue mud: residue sand were incubated for four weeks and a portion was then leached bi-weekly for another 14 weeks. The macroporosity of sand was much greater than that of mud whilst available water holding capacity was greater for mud. Adding increasing proportions of sand to mud decreased total porosity but increased macroporosity although the increase was only appreciable with the presence of 75% sand. The Western Australian residues had a higher Si and quartz content (48% quartz for sand) than north Queensland residues reflecting the lower grade of parent bauxite ore in Western Australia. The content of amorphous minerals and the residual acid neutralizing capacity were lower in Western Australian residues. Due to seawater neutralization of north Queensland residues, they had a greater EC and exchangeable Ca, Mg, K and Na content and lower ESP and pH (9.3 compared to 11.0-11.3) than those from Western Australia. Leaching caused a decrease in the EC of residues by at least one order of magnitude and ammonium acetate-extractable Na levels were reduced by more than half. The pH of leachates from West Australian residues tended to decline with time and the pH of the residue also declined. This was attributed to leaching of HCO_3^-/CO_3^{2-} (soluble alkalinity) with the mobile Na^+ ion. The pH in leachates from north Queensland residues increased progressively until they were about two units higher than initial values and the pH of residues also increased. This was attributed to dissolution of solid phase alkalinity present in the residue. It was concluded that chemical constraints to revegetation

will be much greater for north Queensland mud than West Australian sand, and the strategies should be site specific.

Keywords: bauxite processing mud, bauxite processing residue, red mud, leaching.

3.1 Introduction

Australia is the world's largest miner of bauxite and generates about 30% of the global alumina production (Geosciences, Australia, 2015). The two main bauxite deposits currently being mined and refined in Australia are in far north Queensland and in south-Western Australia. Both deposits are lateritic in origin, the main ore mineral present is gibbsite and both are shallow deposits mined by open cut techniques (Loughnan and Bayliss, 1961; Anand et al., 1991). Nonetheless, while the north Queensland deposit is one of the world's highest grade deposits (49-53% Al_2O_3), by contrast the Western Australian deposit has a lower Al content (27-30% Al_2O_3) than most other deposits mined on a commercial scale throughout the world. Despite this, the Western Australian deposit accounts for over 70% of Australia's alumina production. The reason is that this bauxite deposit contains little reactive Si (i.e. layer silicate clay minerals) and most of the silica is present as quartz which is relatively insoluble during Bayer digestion (Anand et al., 1991).

The Bayer process is used to extract alumina by dissolving bauxite ore in hot NaOH (Power et al., 2011). For every tonne of alumina extracted, 1-2 tonnes of alkaline, saline/sodic bauxite processing residues are produced (Jones and Haynes, 2011). Because of its lower grade, more residue is produced from Western Australian than north Queensland bauxite. Bauxite residues can be separated into residue sand (> 150 um) and residue mud (< 150 um) and the preponderance of quartz in the Western Australian deposit results in a much larger proportion of residue sand (> 30%) being produced than from north Queensland bauxite (< 5%).

In Western Australian the residue mud is dry stacked (50% solids) between gently sloped embankments constructed from residue sand (Cooling, 2007; Power et al., 2011). After additions of gypsum and fertilizers the sand is revegetated with plants native to a coastal sand dune ecosystem in a Mediterranean climate. The north Queensland refineries do not separate the mud from the small amount of sand present but deposit residue (after seawater neutralization) by semi-dry stacking (30% solids) between soil-based retaining walls. Although research into revegetation of Western Australian residue sand is well advanced (Eastham et al., 2006; Banning et al., 2011; Jones et al., 2012a, b), to date, there are no reports on revegetation of seawater-neutralized mud residues. In order to improve the water holding capacity of residue sand before its revegetation, it has been suggested that residue

mud can be added (Anderson et al., 2011) while residue sand is often added to mud before its revegetation in order to improve aeration, drainage and root penetration (Courtney and Timpson, 2004; Courtney et al., 2009).

Research previously carried out at this laboratory (Jones et al., 2010, 2011, 2012a, b, 2015) has concentrated on revegetation strategies for bauxite residue sand from the Western Australian bauxite deposit. Future research will focus on the properties and revegetation of seawater neutralized residue mud from the north Queensland deposit. The purpose of this study was, therefore, to compare the properties of these two materials and investigate the effect of adding residue sand to mud (or mud to sand) on soil chemical and physical properties of the substrate using mud and sand from the Western Australian and north Queensland deposits. The combinations used were: 100% mud, 75% mud/25% sand, 50% mud/50% sand, 25% mud/75% sand and 100% sand.

3.2 Materials and methods

3.2.1 Samples and Experiment Design

Bauxite residues were obtained from an alumina refinery in north Queensland and one in Western Australia. The mud and sand at the north Queensland refinery were separated and collected by hand sieving the residue slurry immediately following seawater neutralization and prior to their deposition in the residue disposal area. The sand made up approximately 3% of the total residue mass. The Western Australian mud and sand were collected immediately after deposition in the disposal area. The sand made up approximately 30% of the total residue mass. Sieve analysis showed that particle size distribution of north Queensland residue sand was: > 1 mm, 2.3%; 0.5-1 mm, 17.6%; 0.25-0.5 mm, 43.8%; 0.125-0.5 mm, 34.4%; < 0.125 mm, 1.9% and for the Western Australian residue sand it was: > 1 mm, 7.8%; 0.5-1 mm, 24.6%; 0.25-0.5 mm, 36.0%; 0.125-0.5 mm, 21.5%; < 0.125 mm, 10.1%. The Western Australian mud had a particle size distribution of < 2 µm 24%, 2-20 µm 54%, and 20-200 µm 22%.

For each residue source, five treatments were prepared consisting 0:100, 25:75, 50:50, 75:25 or 100:0% v/v residue mud: residue sand. Samples (1 kg dry weight) were thoroughly mixed, rewetted to 70% water holding capacity and incubated for four weeks (to allow time for equilibration) in a randomized block design with three replicates. A subsample was air-dried for subsequent chemical analysis while part of the moist sample was used for measurement of physical parameters and another (200 cm^3) was transferred to polypropylene leaching tubes (12 cm long and 5 cm diameter). A plug of glass wool was placed at both the top and bottom of the incubation column to prevent loss of material by downward movement of fine particles during leaching. Samples were incubated for two weeks and

then leached slowly (over a 24 h period) with one pore volume of distilled water. One pore volume approximates to about 1.9 times the mean weekly rainfall at the site of the refineries in north Queensland (i.e. 18 mm) and 2.3 times the mean weekly rainfall at the site of the refinery in Western Australia (i.e. 15 mm). Leachate was collected in polypropylene collecting containers and stored at 5 ºC until analysed. Following leaching, a tension of 17 kPa was applied to each column for 10 minutes to remove excess water. This process was repeated every two weeks for seven leachings. At the completion of leaching, residue was removed from tubes and air-dried for subsequent chemical analysis.

3.2.2 Chemical analysis

In order to determine their mineralogy, residues were subjected to X-ray diffraction analysis. Amorphous content was calculated by difference using a corundum internal standard of known amorphous content. Exchangeable bases (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) were extracted with 1M ammonium acetate (pH 7.0) (Rayment and Higginson, 1992) analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). EC and pH were analysed in a 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson, 1992). Extractable Al was extracted with 1M KCl at (1:10 ratio for 1 h) and Al analysed by ICP-MS. Saturated paste extracts were prepared (Rhoades, 1982) and extracted under vacuum. The pH and EC in extracts were measured using a glass electrode and Ca, Mg, K, Na and Al by ICP-AES. For unleached samples, exchangeable Ca, Mg, K and Na concentrations were calculated by subtracting the concentrations in saturated paste extracts from those in the ammonium acetate extracts (Jones et al., 2012a). Effective cation exchange capacity was calculated as the sum of exchangeable cations (Ca, Mg, K and Na). Exchangeable sodium percentage (ESP) was calculated as the percentage of exchangeable bases present as Na. Bicarbonate-extractable P was extracted with 0.5M $NaHCO_3$ (pH 8.5) (1:100 w/v ratio for 16 h) (Colwell, 1963) and measured colorimetrically by the molybdenum blue method. Diethylenetriaminepentaacetic acid (DTPA)-extractable metals were extracted according to Lindsay and Norvell (1978) (0.005M DTPA, 0.01M $CaCl_2$ and 0.1M TEA: 1:2 ratio for 2 h) and Zn, Cu, Mn, Fe, Pb, Cd and Cr were analysed by ICP-MS. Acid neutralizing capacity of mud and sand samples before and after leaching was measured by titrating a mud/water slurry to pH 7.0, using 0.5M HCl, over a 24 and 120-hour period. Short term (24 h) and residual (120-24 h) acid neutralizing capacity (mol H^{+} kg^{-1} solid) was calculated (Snars et al., 2004). These two fractions represent easily soluble alkalinity and solid phase residual alkalinity.

The total content of P, K, Ca, Mg, Si and heavy metals in residue mud and sand was determined by ICP-AES after microwave digestion using HF, HCl and HNO_3. Total C and N were measured by dry

combustion using a Carlo Erba C, H, N analyser (Rayment and Higginson, 1992). In order to calculate the organic C content of residues, inorganic C (HCO_3^-/CO_3-C) was removed from samples by treatment with 1M HCl to lower pH to 4.0 over a 4-day period (with intermittent vigorous mixing) prior to total C analysis (see above). Residual acid was neutralized by raising pH to 5.0 using 0.5M NaOH and the samples were dried at 50 ºC before TOC analysis. Leachates were analysed for Al, Ca, K, Mg, Na, P (ICP-AES) and pH and EC using a pH/conductivity meter.

3.2.3 Physical analysis

Bulk density was determined on naturally compacted samples (Haynes and Goh, 1978), particle density by the pycnometer method (Blake and Hartge, 1986) and total porosity by difference (Danielson and Sutherland, 1986). Pore size distribution was calculated as macropores (> 29 µm diameter, air-filled pores at -10 kPa), mesopores (0.2-29 µm diameter, drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter, water-filled pores at -1500 kPa). Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Field capacity was determined as the volumetric water content at -10 kPa and available water as that held between -10 and -1500 kPa.

3.2.4 Germination assay

A germination assay was carried out (in quadruplet) on residues before and after leaching using filter paper in petri dishes. Five mL of aqueous extract (1/10 w/v) from residues was added to dishes (Belyaeva and Haynes, 2009). Ten seeds of watercress (*Lepidium sativum*) were placed on filter paper and dishes placed in the dark at 25 ºC. The germination percentages with respect to control (distilled water) and root lengths were determined after 5 days. The germination index (GI) was calculated as $GI = \%G \times Le/Lc$, where $\%G$ is the percentage of germinated seeds in each extract with respect to control, Le is the mean total root length of the germinated seeds in each extract, and Lc is the mean root length of the control (Belyaeva and Haynes, 2009). The control GI value is considered as 100%.

3.2.5 Statistical analysis

The statistical significance of experimental treatments was determined by subjected the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test.

3.3 Results

3.3.1 Elemental and mineralogical composition

The elemental and mineralogical composition of the residues is shown in Table 3.1. The pH of north Queensland residues was less, and the EC greater than those from Western Australia. North Queensland residues had a greater Na and Mg and lower Si content than Western Australian residues and for both residue sources sand had a higher Si and lower Na, K, Mg, Ca, Al and P content than mud. Between 23 and 42% of the mineral content of the residues was amorphous (Table 3.1). Mud samples had a higher amorphous content than sand and north Queensland residues had a higher content than those from Western Australia. The crystalline mineralogy of north Queensland residues was dominated by hematite and sodalite and that of Western Australia by goethite, hematite and quartz. For both residues, sand had a greater content of quartz than mud and for Western Australian residue, sand content was notably high (47.6%).

3.3.2 Carbon content and extractable micronutrients

The organic C content of residues was considerably less than the total C content (Table 3.2) due to the presence of inorganic C (HCO_3^-/CO_3^{2-}) in residues. This effect was more marked for Western Australian residues (Table 3.2) which had a higher pH and therefore a greater HCO_3^-/CO_3^{2-}) content. DTPA-extractable Cu and Mn were greater and Fe less in north Queensland than Western Australian residues while extractable Zn concentrations were similar for the two residue sources.

3.3.3 *pH, EC, exchangeable and saturation paste cations and extractable P*

The pH and EC of both saturation paste (Table 3.3) and water extracts (Table 3.4) were similar in all combinations of mud and sand and the pH was lower and EC higher in north Queensland than Western Australian residues. The Ca, Mg, K and Na concentrations in saturation paste (Table 3.3) and ammonium acetate extracts before leaching (Table 3.5) were markedly higher in north Queensland than Western Australian residues while the reverse was the case for Al, SAR and ESP before leaching (Tables 3.3, 3.4 and 3.5). For north Queensland residues, the Mg in saturation paste and ammonium acetate extracts (before leaching) was greater in sand than mud while the reverse was the case for Ca, K and Na. For Western Australian residues, Na, K and Ca in saturation paste extracts (Table 3.3) were lower for sand than mud and before leaching, ammonium acetate extracted more Ca and less Mg and Na from sand than mud (Table 3.5). After leaching, concentrations of cations in saturation paste extracts were very low being < 70, 0.70, 0.30 and 0.02 $mmol_c\ kg^{-1}$ for Na, K, Mg and Ca

respectively and the EC was < 2.4 dS m^{-1} (data not presented). Colwell-extractable P was much greater in Western Australian than north Queensland mud (Table 3.4).

3.3.4 Correction of exchangeable cation values

For unleached residues, subtraction of soil solution cations (i.e. cations in saturation paste extracts) from ammonium acetate-extractable cations is necessary to obtain an estimate of cations held on cation exchange sites (and thus ECEC). Subtraction of solution cations lowered the calculated ECEC (c.f. Table 3.2 and Table 3.4, initial unleached values) by 66-69% for north Queensland and 46-62% for Western Australian residues. This was mainly due to the reductions in estimated exchangeable Na (being the dominant cation present) (Table 3.3) although estimates of exchangeable Ca, Mg and K also decreased (data not shown). Values for ESP were also lowered (c.f. Tables 3.2 and Table 3.4, initial unleached values) because Na is held the least strongly of any of the cations.

3.3.5 Effect of leaching

Leaching caused a decrease in EC of at least one order of magnitude for both residue sources, significant increases in pH for north Queensland residues and a decrease in pH for Western Australian residues (Table 3.4). There was a substantial decrease in exchangeable Na (and consequently calculated ECEC) for both residues following leaching (Tables 3.4 and 3.5). There was also a decrease in exchangeable Mg, Ca and K for north Queensland residues and a tendency for the same trend for those from Western Australia. For Western Australian residues, leaching also caused a decrease in extractable Al (Table 3.5) and ESP (Table 3.4).

3.3.6 Composition of leachates

Over time the pH of leachates from the north Queensland residues increased progressively while that for Western Australian residues remained relatively constant and then tended to decline after the fifth leaching event (Fig. 3.2). The EC of leachates declined rapidly with increasing time (Fig. 3.2). For simplicity, the concentrations of Na, Ca, K, Mg, Al and P in leachates over time are shown for only the mud and sand samples (Fig. 3.1) but mean concentrations of these ions in leachates for all treatments are presented in Table 3.6. There was a rapid decline in Na concentrations with time for both residue sources and this also occurred for Ca and Mg in north Queensland residues (Fig. 3.1). The decline in K concentrations for north Queensland residues was less rapid while concentrations of P in leachates from Western Australian mud slowly declined with time (Fig. 3.1). There were notable concentrations of Al in leachates from Western Australian residues and while those for mud

tended to increase over the first four leachings those for sand remained relatively constant over the seven leaching events.

3.3.7 Acid neutralizing capacity

In order to help explain the changes in pH during leaching, the acid neutralizing capacity of mud and sand before and after leaching was measured (Fig. 3.3). Both short-term and residual acid neutralizing capacity were greater for mud than sand. Short-term acid neutralizing capacity of north Queensland mud was less than that for Western Australian mud prior to leaching. After leaching of alkalinity from the Western Australian mud, it had a similar short-term acid neutralizing capacity to that from north Queensland (Fig. 3.3). The residual acid neutralizing capacity of mud and sand from north Queensland was greater than that from Western Australia.

3.3.8 Physical properties

For both residue sources, sand had a greater bulk density and lower total porosity than mud and for all combinations of mud and sand mesoporosity dominated pore size distribution (Table 3.7). Increasing sand additions increased macroporosity with a concomitant decrease in mesoporosity for north Queensland residues and a decrease in both meso- and microporosity for Western Australian residues. However, macroporosity was not increased to above 10% until the 75% sand addition to mud (Table 3.7). Progressive additions of sand to mud decreased both available water and water held at field capacity.

3.3.9 Germination index

Prior to leaching, germination percentage was similar in north Queensland residues for all combinations of mud and sand (69-74%) but for Western Australian residues, germination was greatly reduced in mud and progressively increased with increasing sand additions (Table 3.4). Following leaching, germination index was increased at 75% and 100% sand for north Queensland residue and at 0, 25, 50 and 75% sand for Western Australian residues. Both before and after leaching, the highest germination percentage was recorded for Western Australian sand.

3.4 Discussion

3.4.1 Properties of the residues

The elemental and mineralogical content of residues is a reflection of the nature of the parent ore, inputs and transformations that occur during the Bayer process plus any subsequent neutralization reactions. The lower Al content of the bauxite from the Western Australia compared with the north Queensland deposit was reflected in its much greater quartz and Si content for both the mud and sand. As a result of the higher content of unreactive quartz, sand particles had a lower ECEC than mud and this effect was more pronounced for the Western Australian sand (which was composed of 48% quartz). This low ECEC means that retention of exchangeable cations by the material will be poor unless other materials with a higher CEC (e.g. residue mud or organic wastes such as biosolids) are added to the sand prior to revegetation. Grafe et al. (2011) reported that the mineralogy of residues typically contains about 70% crystalline phases and 30% amorphous materials and in agreement with this, residues contained between 23 and 42% amorphous material. The higher content of amorphous material for north Queensland residues is a possible source of residual alkalinity (see below).

Sodalite (also known as desilication product) is a sodium aluminium silicate mineral formed during the Bayer process which contributes to a slow release of Na^+ and OH^- ions from bauxite residues over time during storage (Barrow, 1982; Wong and Ho, 1995; Menzies et al., 2009). This pool of residual alkalinity, present in the north Queensland residue in significant quantities, means that although the residue was seawater neutralized (to a pH of around 9.0 compared to 11.0-11.3 for Western Australian residues) (Table 3.1) an increase in pH and exchangeable Na is likely to occur in the longer term, during storage (Menzies et al., 2009). The lack of detectable sodalite in Western Australian sand means that the material has less alkaline buffering capacity and this will potentially increase the ease of revegetation.

Seawater neutralization results in the replacement of some of the Na^+ on exchange sites with Ca^{2+}, Mg^{2+} and K^+ (from the seawater) and a consequent decrease in Na saturation. As a result, north Queensland residues had a higher initial content of Ca, Mg and K in ammonium acetate and saturation paste extracts (and a lower ESP) than those from Western Australia. During seawater neutralization, fine mud particles (< 5 µm dia.) flocculate into larger agglomerates (80-400 µm) (Hanahan et al., 2004; Palmer et al., 2009) and the displaced cations, and those originating from the seawater, can accumulate within the agglomerates. For that reason, cations and EC in saturation paste extracts were particularly high in the north Queensland mud.

Another consequence of seawater neutralization is the precipitation of soluble alkalinity as sparingly soluble Ca and Mg hydroxides and hydroxycarbonates (e.g. hydrotalcite) and a consequent decrease in pH (Hanahan et al., 2004; Palmer et al., 2009). As a result, inorganic C content (HCO_3^-/CO_3^{2-}) and the short-term acid neutralizing capacity (caused by the presence of HCO_3^-/CO_3^{2-}) of north

Queensland mud were markedly less than that from Western Australia. However, X-ray diffraction analysis did not detect crystalline compounds such as hydrotalcite suggesting they are present in non-crystalline form within the significant amorphous mineral content of the north Queensland residues. It is important to note that the alkalinity associated with the newly-precipitated solid phase is still present in the residue and can potentially be released over time as the materials re-dissolve (causing a pH increase).

Western Australian residue mud had a notably high Colwell extractable-P content (i.e. 116.9 mg kg^{-1}) which is higher than many fertile agricultural soils (Moody and Bolland, 1999). This is because the bauxite from Western Australia is high in P (it contains 195 mg P kg^{-1}) and during the refining process used, P is added as dihydrogen phosphate to control calcia (Carter, 2006; Phillips and Chen, 2010). Thus, although the mud is high in Fe oxides (which characteristically adsorb and sequester P) the extractable P content is still very high. By contrast, the north Queensland mud had an extractable P content of 15.7 mg kg^{-1} which would be considered low for agricultural soils (Moody and Bolland, 1999). In agreement with this, the amounts of P leached were much greater from the Western Australian residues.

The EC values in saturation paste extracts prior to leaching were very high ranging from 28-34 dS m^{-1} for north Queensland residue and 5.2-13.2 dS m^{-1} for Western Australian residue. An EC of > 2 dS m^{-1} is considered saline and values > 12 dS m^{-1} are generally considered too saline for most plants (Shaw, 1999). Such values underline the importance of allowing time for leaching of salts out of the profile prior to revegetation. Indeed, the very high EC in seawater neutralized residue, originating from the seawater, means that leaching is essential prior attempting to revegetate the residue. The residues were also sodic as shown by corrected ESP values which ranged from 37-92% and SAR values of 72-604. Even after leaching, ESP values ranged from 22-70% for Western Australian and 68-82% for north Queensland residues. ESP values above 10-15% and SAR values above 13 are normally considered likely to reduce plant growth (Sumner, 1993). The lower exchangeable Na and ESP values for Western Australian than north Queensland residues are due to the higher content of relatively inert quartz material in Western Australian material which dilutes out the Na held on exchange sites of the reactive Fe oxides in the residue. Thus, although tolerance to Na can differ greatly between plant species, sodicity in all of the residue samples is likely to limit plant performance. A common practice prior to revegetation is to add gypsum ($CaSO_4 \cdot 2H_2O$) to the residue. As well as resulting in some precipitation of alkalinity as calcite, the added Ca^{2+} displaces exchangeable Na^{+} which leaches down the profile with the added SO_4^{2-} (Jones and Haynes, 2011). As a result, EC, SAR and ESP are greatly reduced and such a practice would be highly desirable when revegetating these materials.

In addition, fertilizer additions of nutrients such as N, K, Mg, Mn and Zn will also be needed. For example, critical levels of exchangeable K and Mg for adequate plant growth are about 0.2-0.5 and 0.14-0.30 $cmol_c\ kg^{-1}$ respectively (Aitken and Scott, 1999; Gourley, 1999) so that after leaching levels of extractable K were low in north Queensland residues and extremely low in Western Australian residues while Mg status was very low for Western Australian sand. Critical levels of DTPA-extractable Fe, Mn, Zn and Cu are about 4.5, 1.0, 0.8 and 0.2 mg kg^{-1} (Lindsay and Norvell, 1978) so that concentrations of Mn and Zn were low in both residues, Fe was low in north Queensland residues and Cu was low in the Western Australian sand. The extremely low organic matter content of residues also means fertilizer N is essential (Eastham et al., 2006).

Calculated ECEC values prior to leaching were reduced greatly when cation concentrations in saturation paste extracts were subtracted and this effect was particularly evident for the seawater neutralized north Queensland mud (which had a high EC and very high concentrations of Na in saturation paste extracts). Corrected ESP values were also lowered because soil solution Na represented a proportionately greater percentage of the total ammonium acetate-extractable pool than that for other cations such as Ca and Mg (since monovalent cations are held less strongly than divalent ones) (Brady and Weil, 2007). After leaching, soluble salts were low and correction of ECEC/ESP was not necessary.

3.4.2 Effects of leaching

A decrease in pH for Western Australian residues during leaching has been noted previously and can be attributed to leaching of HCO_3^-/CO_3^{2-} (soluble alkalinity) as counterions for the mobile Na^+ ion (Jones et al., 2012b, 2015). The marked increase in pH of leachates and in residues during leaching of north Queensland residues is due to dissolution of solid phase alkalinity. It is notable that the residual acid neutralizing capacity of north Queensland residues was greater than that for Western Australian residues reflecting a greater residual alkalinity. As noted above, there are several possible sources of such alkalinity in north Queensland residues including previously precipitated amorphous hydrotalcite as well as sodalite. Indeed, Menzies et al. (2009) suggested that dissolution of sodalite was the main source of residual alkalinity causing an increase in pH when a seawater neutralized sample of bauxite residue sand was leached with fresh water. Another possible source is tricalcium aluminate hexahydrate (TCA) which is formed when lime is added to Bayer liquor and this also accumulates in the mud (Khaitan et al., 2009; Grafe et al., 2011). This compound was not found by X-ray diffraction but it is presumed to be present within the amorphous mineral component. Indeed, the substantial amorphous phase of the mineral component of the residue may well contain

amorphous precursors for minerals such as hydrotalcite, sodalite and TCA and therefore contribute appreciably to residual alkalinity. That is, amorphous minerals are likely to be considerably more soluble than their thermodynamically stable crystalline counterparts. The contribution of the amorphous phase to residual alkalinity therefore needs further characterization.

A proposed advantage of seawater neutralization is that the pH of mud is decreased appreciably and this will result in leachates with a lower pH. Such leachates should therefore have much less potential for environmental damage. However, results presented here suggest that the pH of leachates will increase with time although are still less than those from non-neutralized residues.

3.4.3 Physical properties

As noted above, during seawater neutralization, mud particles flocculate into larger agglomerates (Hanahan et al., 2004) and this has been observed to result in a decreased bulk density and increased hydraulic conductivity (Rai et al., 2013). In agreement with this, bulk density was less and total porosity greater for north Queensland than Western Australian residues. For both residue sources, sand had a much greater macroporosity than mud but addition of sand to mud only had a substantial effect on macroporosity when the mixture contained 75% sand. Indeed, additions of small amounts of sand (e.g. 25%) tended to reduce total porosity and had no significant effect on pore size distribution. The decrease in total porosity is attributable to the ability of small mud particles to fill macropore voids between sand particles. Additions of sand to mud at 25% are common practice (Courtney et al., 2009) but results presented here suggest they have little effect on measured physical properties of the medium.

3.4.4 Germination index

For both residue sources, germination tended to be lower in mud than sand and this effect was particularly marked in Western Australian residues prior to leaching. After leaching, there was still significant inhibition of germination in mud (and mixtures containing a substantial amount of mud) from both residue sources and mud had greater ESP values than sand. As already noted, a reduction in ESP can be achieved by adding gypsum followed by leaching. Indeed, although germination percentage was satisfactory (> 65%) in all residues after leaching, plants are unlikely to grow satisfactorily in these materials (ESP of 20-82%). Patterns for seed germination versus subsequent growth of plants in bauxite residues are often dissimilar (Jones et al., 2012a) since longer-term

physiological effects of salinity/sodicity on plant growth are not assayed in short-term germination tests.

3.4.5 Practical implications

Western Australian sand, which is routinely separated from the mud fraction has a high silica/quartz content, the lowest EC and short term and residual acid neutralizing capacity as well as lowest Na content of any of the materials examined. In addition, it had the greatest macroporosity. After field neutralization with gypsum and leaching it is therefore the most suitable material for revegetation although it has a low water holding capacity and the low CEC means cation retention is low. Thus, because of its properties and availability, the material is presently used successfully for revegetation.

Since the sand represents less than 5% of the residue produced from the north Queensland deposit, it is the mud component which will be revegetated at the north Queensland. This will present considerable challenges in comparison with revegetation of sand from Western Australia. Amendment of the mud with organic materials to improve physical properties will be desirable. Although seawater neutralization has lowered pH to about 9.0, the salinity is very high and it still has a high Na content (> 68% Na saturation). Displacement of Na (e.g. with a source of Ca such as gypsum and/or organic waste) and subsequent leaching of salts will be necessary. The increase in pH (of both the mud and of leachates) that occurs during leaching of this seawater neutralized residue needs further investigation and the source of residual alkalinity responsible deserves future investigation.

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Table 3.1 *pH, EC, elemental and mineralogical composition of the materials used.*

Residue	pH	EC	Total Analysis (g kg^{-1})							
			Si	Fe	Al	Ca	K	Mg	Na	P
N. Qld mud	9.3	16.51	74	199	64.8	7.8	1.5	3.5	79.6	0.4
N. Qld sand	9.3	7.55	101	247	54.4	2.2	1.1	1.5	57.1	0.3
W. Aust mud	11.0	5.65	104	191	67.1	12.5	7.3	0.6	37.2	0.7
W. Aust sand	11.3	1.35	247	158	50.4	0.8	0.9	0.04	3.3	0.1

Residue	Mineralogical composition (%)												
	Quartz	Hematite	Goethite	Maghemite	Calcite	Anatase	Rutile	Boehmite	Gibbsite	Kaolin	Illite	Sodalite	Amorphous
N. Qld mud	1.2	29.0	2.0	1.2	2.2	2.2	1.3	5.7	0.2	-	-	10.9	41.9
N. Qld sand	7.0	33.6	3.7	2.8	0.6	0.7	0.8	7.5	0.3	0.6	-	9.4	32.4
W Aust mud	7.1	8.5	22.2	-	6.5	0.6	0.6	3.3	1.3	-	11.7	4.1	34.2
W. Aust sand	47.6	11.2	9.9	0.9	0.2	0.1	0.5	0.4	4.3	0.5	0.8	-	23.4

Table 3.2 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on total and organic C, DTPA-extractable micronutrients and corrected (ammonium acetate minus saturation paste) exchangeable Na, ECEC and ESP.*

Residue	Sand addition (% v/v)	Total C (g kg^{-1})	Organic C (g kg^{-1})	DTPA – extractable metal (mg kg^{-1})				Exchangeable Na ($cmol_c$ kg^{-1})	ECEC ($cmol_c$ kg^{-1})	ESP (%)
				Fe	Mn	Zn	Cu			
N. Qld	0	7.4^{e}	3.1^{f}	0.41^{a}	0.66^{e}	0.25^{a}	1.82^{g}	11.5^{d}	30.8^{d}	36.7^{a}
	25	5.7^{d}	2.7^{de}	0.49^{a}	0.68^{ef}	0.20^{a}	1.38^{f}	11.5^{d}	29.9^{d}	37.3^{a}
	50	5.2^{cd}	2.4^{cd}	0.60^{a}	0.73^{f}	0.23^{a}	1.05^{e}	9.2^{cd}	25.2^{c}	36.5^{a}
	75	4.6^{bc}	2.1^{c}	1.14^{a}	0.88^{g}	0.20^{a}	0.57^{c}	9.6^{cd}	22.9^{c}	41.6^{ab}
	100	3.8^{b}	2.2^{c}	3.16^{b}	1.28^{h}	0.25^{a}	0.21^{b}	10.0^{d}	20.0^{c}	50.0^{b}
W. Aust	0	20.5^{g}	3.7^{g}	21.5^{f}	0.29^{d}	0.31^{a}	1.01^{e}	18.7^{e}	20.2^{c}	92.3^{d}
	25	12.8^{f}	2.8^{ef}	20.7^{f}	0.24^{c}	0.27^{a}	0.76^{d}	12.5^{de}	14.6^{bc}	86.0^{cd}
	50	7.4^{e}	2.2^{c}	17.4^{e}	0.18^{b}	0.25^{a}	0.53^{c}	7.9^{c}	10.3^{b}	76.9^{c}
	75	3.8^{b}	1.8^{b}	11.4^{d}	0.10^{a}	0.21^{a}	0.22^{b}	3.8^{b}	6.8^{ab}	55.5^{b}
	100	2.0^{a}	1.2^{a}	9.21^{c}	0.05^{a}	0.22^{a}	0.06^{a}	1.7^{a}	4.0^{a}	43.5^{ab}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

Table 3.3 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on pH, EC, Al and extractable cations in saturated paste extracts.*

Residue	Sand addition (% v/v)	pH	EC (dS m^{-1})	Saturated paste extractable cations ($mmol_c$ L^{-1})					SAR
				Ca	Mg	K	Na	Al	
N. Qld	0	7.0^{a}	34.1^{f}	50.3^{f}	1.6^{b}	7.7^{c}	698^{e}	0.005^{b}	119^{a}
	25	6.8^{a}	32.3^{ef}	46.5^{f}	4.4^{bc}	7.5^{c}	698^{e}	0.005^{b}	129^{a}
	50	6.8^{a}	31.6^{e}	36.6^{e}	9.6^{cd}	7.0^{bc}	630^{d}	0.004^{ab}	121^{a}
	75	6.9^{a}	30.8^{de}	25.7^{d}	18.9^{d}	6.5^{b}	588^{cd}	0.004^{ab}	107^{a}
	100	6.9^{a}	28.6^{d}	9.0^{c}	24.6^{e}	5.9^{b}	526^{c}	0.003^{a}	72^{a}
W. Aust	0	10.2^{a}	13.2^{c}	0.33^{b}	0.07^{a}	0.32^{a}	225^{b}	0.02^{c}	518^{b}
	25	10.3^{a}	12.8^{c}	0.31^{b}	0.03^{a}	0.28^{a}	225^{b}	0.03^{cd}	586^{bc}
	50	10.4^{ab}	12.2^{b}	0.26^{ab}	0.03^{a}	0.27^{a}	219^{b}	0.04^{cd}	604^{c}
	75	10.5^{ab}	8.26^{ab}	0.22^{a}	0.02^{a}	0.22^{a}	175^{ab}	0.05^{d}	556^{bc}
	100	10.6^{b}	5.15^{a}	0.15^{a}	0.01^{a}	0.16^{a}	117^{a}	0.06^{d}	512^{b}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

Table 3.4 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on Colwell P, pH, EC, ESP, ECEC and germination index.*

Residue	Sand addition (% v/v)	Colwell P (mg P kg^{-1})		pH		EC (dS m^{-1})		ESP (%)		ECEC ($cmol_c$ kg^{-1})		Germination index (%)	
		Initial	Final	Initial	Final	initial	Final	Initial	Final	Initial	Final	Initial	Final
N. Qld	0	15.7^{cd}	18.6^{d}	9.4^{a}	9.9^{a}*	161^{j}	1.4^{f}*	73^{a}	82^{h}*	98.6^{j}	41.0^{e}*	69^{c}	75^{a}
	25	12.0^{c}	13.0^{c}	9.3^{a}	10.0^{a}*	13^{i}	1.0^{ef}*	74^{a}	78^{g}*	87.6^{i}	40.2^{e}*	74^{c}	68^{a}
	50	7.8^{bc}	9.7^{c}	9.3^{a}	10.2^{a}*	10^{h}	0.81^{d}*	73^{a}	74^{fg}	77.5^{h}	38.6^{e}*	78^{c}	72^{a}
	75	4.1^{b}	1.9^{b}	9.4^{a}	10.3^{a}*	8.9^{g}	0.72^{cd}*	74^{a}	71^{f}	68.5^{g}	38.3^{e}*	71^{c}	91^{c}*
	100	0.7^{a}	0.1^{a}	9.4^{a}	10.5^{a}*	7.6^{f}	0.61^{c}*	75^{a}	67^{e}	59.7^{f}	38.0^{e}*	71^{c}	93^{c}*
W. Aust	0	116.9^{g}	80.6^{g}*	11.0^{b}	10.2^{a}*	5.6^{e}	1.0^{ef}*	95^{d}	69^{ef}*	37.7^{e}	15.3^{d}*	10^{a}	86^{b}*
	25	77.6^{f}	57.8^{f}*	11.0^{b}	10.2^{a}*	4.8^{d}	0.94^{e}*	93^{cd}	62^{d}*	29.0^{d}	11.5^{c}*	12^{a}	83^{b}*
	50	48.7^{e}	37.4^{e}	11.0^{b}	10.1^{a}*	3.6^{c}	0.61^{c}*	90^{c}	49^{c}*	22.2^{c}	8.1^{bc}*	30^{b}	94^{c}*
	75	19.9^{d}	21.5^{d}	11.0^{b}	10.0^{a}*	2.5^{b}	0.39^{b}*	85^{b}	33^{b}*	17.7^{b}	5.5^{b}*	72^{c}	94^{c}*
	100	0.5^{a}	9.1^{c}	11.3^{b}	9.9^{a}*	1.4^{a}	0.13^{a}*	77^{a}	22^{a}*	11.7^{a}	2.8^{a}*	90^{d}	120^{d}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.
* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 3.5 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on ammonium acetate-exchangeable cations and extractable Al before (initial) and after (final) leaching.*

Residue	Sand addition (% v/v)	Exchangeable cations ($cmol_c\ kg^{-1}$)								Extractable Al ($cmol_c\ kg^{-1}$)	
		Ca		Mg		K		Na			
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
N. Qld	0	19^{g}	6.3^{d}*	6.6^{d}	5.4^{g}*	1.0^{c}	0.33^{b}*	72^{g}	29^{e}*	0.04^{a}	0.04^{b}
	25	16^{fg}	5.9^{d}*	6.5^{d}	5.0^{g}*	0.99^{c}	0.34^{b}*	65^{f}	29^{e}*	0.02^{a}	0.04^{b}
	50	13^{f}	5.7^{cd}*	6.6^{d}	3.6^{f}*	0.88^{bc}	0.33^{b}*	57^{ef}	29^{e}*	0.01^{a}	0.01^{c}
	75	9.2^{e}	5.5^{cd}*	7.5^{e}	2.4^{e}*	0.81^{b}	0.34^{b}*	51^{e}	30^{e}*	0.01^{a}	0.02^{a}
	100	6.2^{d}	4.9^{c}*	7.7^{e}	1.8^{e}*	0.78^{b}	0.32^{b}*	45^{e}	31^{e}*	0.01^{a}	0.01^{a}
W. Aust	0	0.9^{a}	0.7^{a}	0.79^{c}	0.56^{d}*	0.05^{a}	0.02^{a}*	36^{d}	14^{d}*	0.19^{b}	0.05^{b}*
	25	1.4^{b}	1.0^{a}	0.55^{bc}	0.44^{c}*	0.04^{a}	0.01^{a}*	27^{c}	10^{c}*	0.19^{b}	0.07^{bc}*
	50	1.8^{bc}	1.3^{a}	0.39^{b}	0.36^{bc}	0.03^{a}	0.01^{a}	20^{bc}	6.4^{b}*	0.20^{b}	0.07^{bc}*
	75	2.4^{c}	1.8^{b}	0.27^{ab}	0.23^{b}	0.03^{a}	0.01^{a}	15^{b}	3.5^{ab}*	0.19^{b}	0.09^{c}*
	100	2.5^{c}	1.9^{b}	0.18^{a}	0.08^{a}	0.03^{a}	0.01^{a}	9^{a}	1.8^{a}*	0.22^{b}	0.10^{c}*

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.
* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 3.6 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on mean ionic composition of leachates over the 7-week leaching period.*

Residue	Sand addition (% v/v)	pH	EC (dS m^{-1})	Mean concentration ($mmol_c$ L^{-1})					
				Na^+	Ca^{2+}	K^+	Mg^{2+}	$Al(OH)_4^-$	$H_2PO_4^-$
N. Qld	0	8.1^a	28.0^c	176.0^d	10.5^c	3.7^b	0.4^a	0.05^a	0.01^a
	25	8.1^a	26.4^c	154.4^d	8.1^c	3.5^b	1.0^b	0.05^a	0.01^a
	50	8.4^a	24.8^{bc}	141.3^d	4.6^{bc}	3.6^b	1.3^b	0.04^a	0.01^a
	75	8.8^a	24.1^{bc}	131.5^c	3.7^{bc}	3.5^b	2.1^{bc}	0.06^a	0.02^a
	100	9.1^a	22.8^{bc}	112.9^b	1.8^b	3.7^b	4.0^c	0.04^a	0.03^a
W. Aust	0	10.3^b	10.5^b	132.7^c	0.09^a	0.2^a	0.1^a	0.07^b	0.6^c
	25	10.4^b	9.2^b	122.3^{bc}	0.07^a	0.2^a	0.2^a	0.06^b	0.5^{bc}
	50	10.4^b	9.0^b	115.3^b	0.06^a	0.2^a	0.2^a	0.08^{bc}	0.3^{abc}
	75	10.5^b	7.0^{ab}	78.4^a	0.05^a	0.1^a	0.01^a	1.0^c	0.1^{ab}
	100	10.6^b	4.9^a	58.1^a	0.03^a	0.1^a	0.01^a	0.6^b	0.04^a

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Table 3.7 *Effect of addition of increasing proportions of residue sand to residue mud [from two sources:north Queensland (N. Qld) and Western Australia (W. Aust))] on physical properties.*

Residue	Sand addition (% v/v)	Bulk Density (mg m^{-3})	Particle Density (mg cm^{-3})	Total Porosity (m^3 m^{-3})	Pore size distribution (%)			Available Water (kg m^{-3})	Field Capacity (kg m^{-3})
					Micropores (< 0.20 µm)	Mesopores (0.20-29 µm)	Macropore (> 29 µm)		
N. Qld	0	0.93^{a}	2.72^{a}	0.66^{c}	34.9^{c}	65.1^{d}	0^{a}	454^{f}	697^{g}
	25	1.04^{ab}	2.68^{a}	0.61^{c}	36.8^{c}	63.2^{d}	0^{a}	405^{e}	643^{f}
	50	1.16^{b}	2.79^{a}	0.59^{c}	36.0^{c}	62.0^{d}	2.1^{ab}	400^{e}	634^{f}
	75	1.16^{b}	2.91^{a}	0.59^{c}	34.5^{c}	48.4^{ab}	17.1^{c}	286^{bc}	490^{de}
	100	1.25^{c}	2.99^{a}	0.58^{c}	35.0^{c}	40.8^{a}	24.2^{cd}	238^{ab}	442^{cd}
W. Aust	0	1.31^{d}	2.89^{a}	0.55^{b}	42.0^{d}	58.0^{c}	0^{a}	357^{d}	615^{f}
	25	1.52^{e}	2.94^{a}	0.47^{ab}	40.7^{d}	59.3^{c}	0^{a}	305^{c}	514^{e}
	50	1.62^{f}	2.93^{a}	0.43^{a}	36.1^{c}	61.3^{cd}	2.6^{b}	264^{b}	420^{c}
	75	1.71^{g}	3.00^{a}	0.41^{a}	23.8^{b}	60.5^{cd}	15.7^{c}	251^{ab}	349^{b}
	100	1.78^{g}	3.05^{a}	0.42^{a}	12.2^{a}	55.0^{b}	32.8^{d}	230^{a}	281^{a}

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Figure Captions

Fig. 3.1. Effect of adding increasing proportions of residue sand to residue mud from two sources [north Queensland (N. Qld) and Western Australia (W. Aust)] on Na^{+}, Ca^{2+}, K^{+}, Mg^{2+}, $Al(OH)_4^{-}$ and $H_2(PO)_4^{-}$ content of leachates during seven progressive leaching events. Standard errors of the means shown.

Fig. 3.2. Effect of adding increasing proportions of residue sand to residue mud from two sources [north Queensland (N. Qld) and Western Australia (W. Aust)] on the pH and EC content of leachates during seven progressive leaching events. Standard errors of the means shown.

Fig. 3.3. (a)Short-term and (b)residual acid neutralizing capacity of residue mud and sand from two sources [north Queensland (N. Qld) and Western Australia (W. Aust)] before and after seven progressive leaching events. Standard errors of the means shown.

Fig.3.1

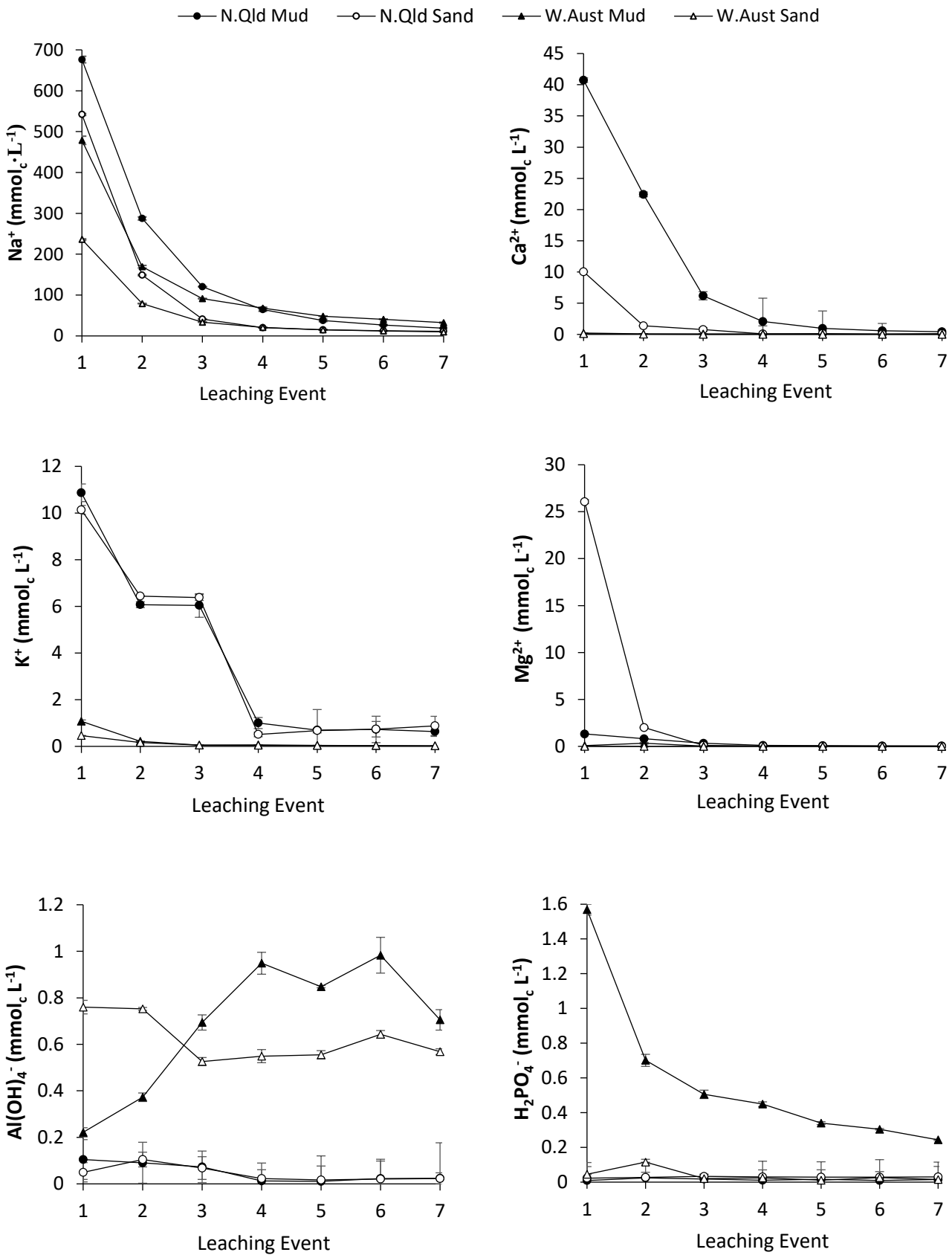

N.Qld Mud
N.Qld Sand
W.Aust Mud
W.Aust Sand
Na+ (mmolc·L-1)
Ca2+ (mmolc L-1)
K+ (mmolc L-1)
Mg2+ (mmolc L-1)
Al(OH)4- (mmolc L-1)
H2PO4- (mmolc L-1)
Leaching Event

Fig. 3.2

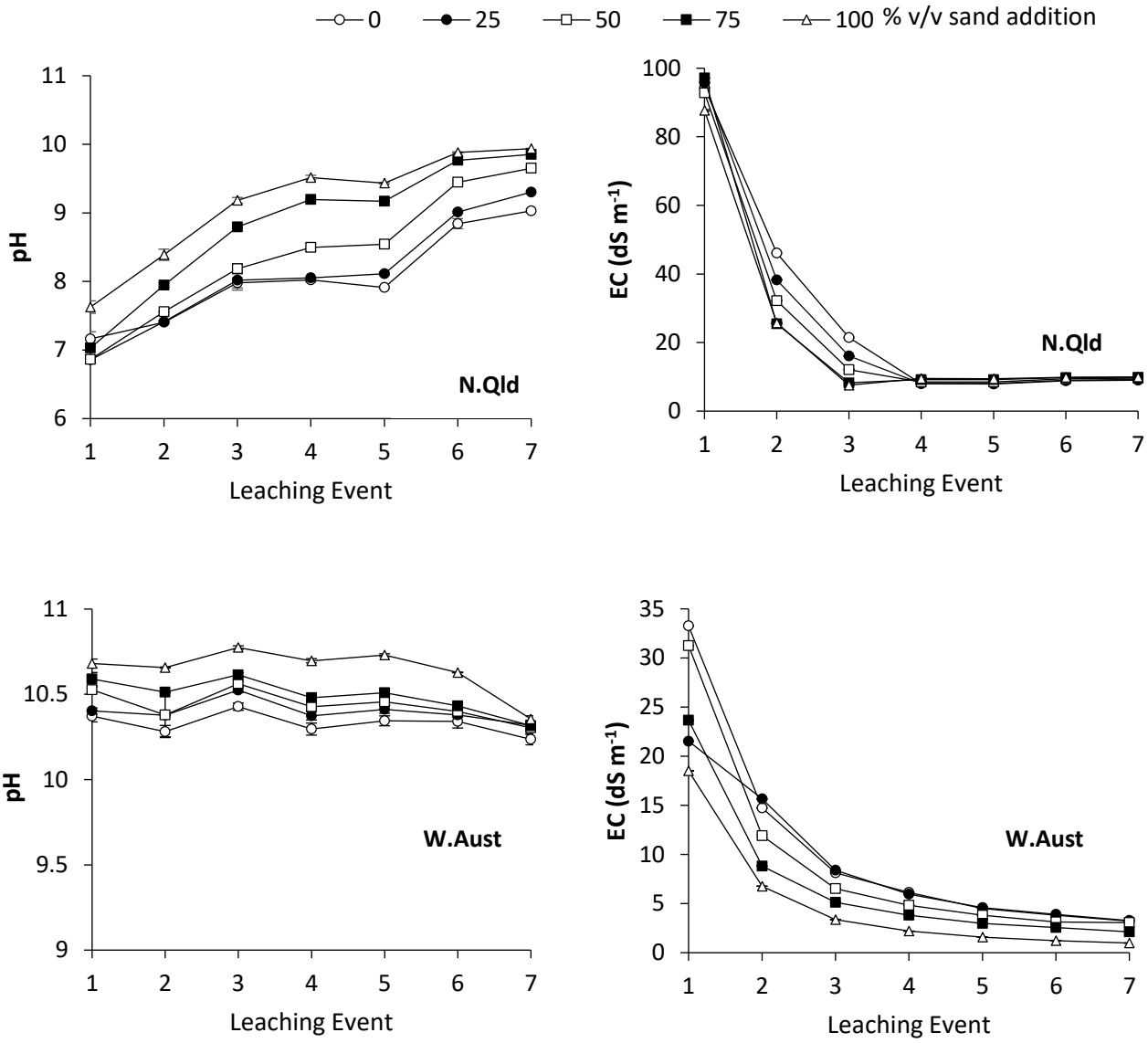
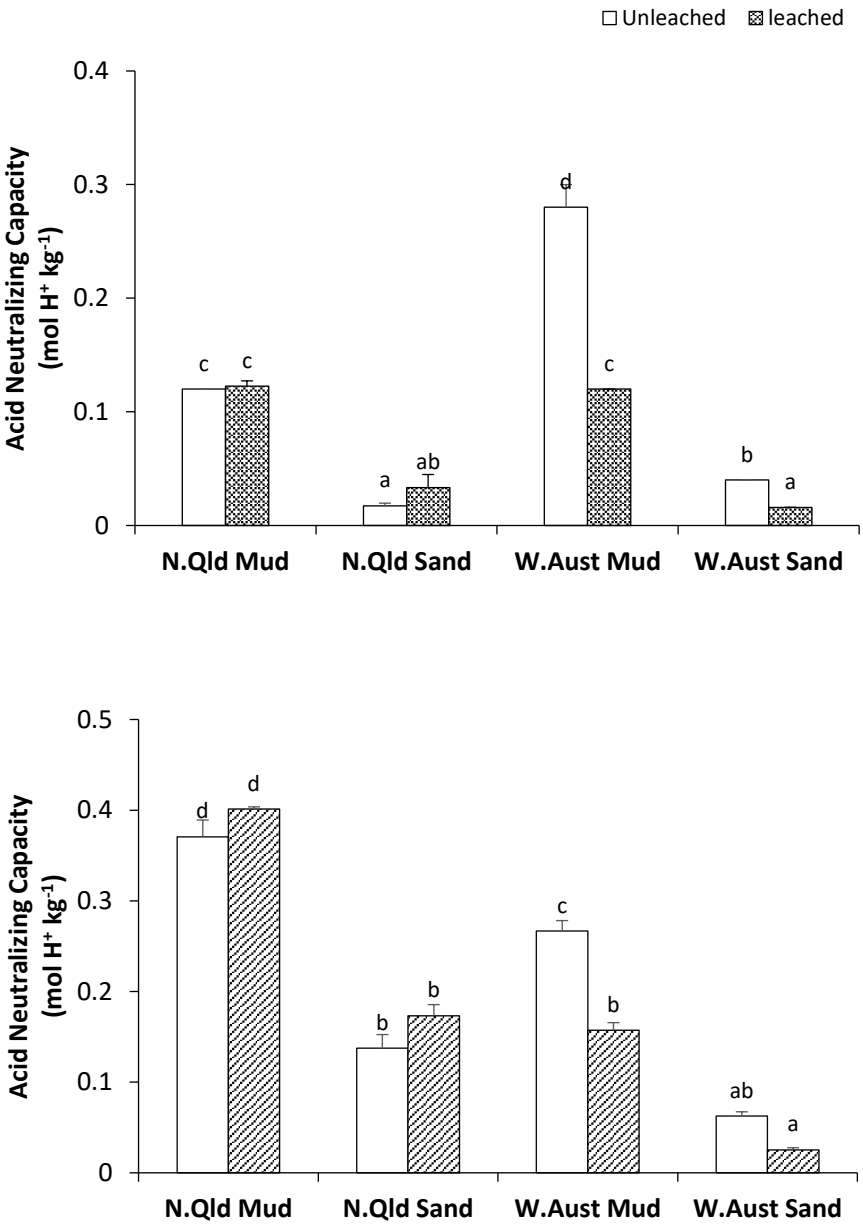

0
25
50
75
100 % v/v sand addition
pH
Leaching Event
N.Qld
EC (dS m-1)
Leaching Event
N.Qld
pH
Leaching Event
W.Aust
EC (dS m-1)
Leaching Event
W.Aust

Fig. 3.3


Unleached
leached
Acid Neutralizing Capacity (mol H+ kg-1)
0.4
0.3
0.2
0.1
0
c
c
a
ab
d
c
b
a
N.Qld Mud
N.Qld Sand
W.Aust Mud
W.Aust Sand
Acid Neutralizing Capacity (mol H+ kg-1)
0.5
0.4
0.3
0.2
0.1
0
d
d
b
b
c
b
ab
a
N.Qld Mud
N.Qld Sand
W.Aust Mud
W.Aust Sand

4. Changes in physical, chemical and microbial properties of seawater neutralized bauxite residue mud induced by additions of residue sand, gypsum and organic matter

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Abstract: Seawater neutralized bauxite residue mud was amended with residue sand (25% v/v), gypsum (1% w/v), poultry manure (6% w/v) and biosolids (6% w/v) and incubated for 4 weeks and then leached with 6 pore volumes of water. It was incubated for another 4 weeks before the chemical, microbial and physical properties were characterized. In a second experiment, the effects of 1% and 5% gypsum application on chemical properties after leaching were measured and compared. After seawater neutralization, the pH of unamended residue was 9.3 but during leaching it rose to 9.6. Addition of 1% gypsum arrested this increase while with 5% gypsum, the pH was lowered to 9.0 after leaching. The major ions in leachates were Na^+ and Cl^- and gypsum application increased the quantities of Na^+, Ca^{2+} and SO_4^{2-} leached. Addition of biosolids increased concentrations of Na^+, Ca^{2+}, K^+ and Mg^{2+} in leachates and poultry manure those of K^+ and Mg^{2+}. Exchangeable and soil solution Ca were increased by addition of gypsum and exchangeable Ca and Mg were also increased by poultry manure and biosolids additions. Exchangeable Na, ESP and SAR were reduced by the addition of gypsum and to a lesser extent by addition of both poultry manure and biosolids. Addition of amendments had small effects on physical properties with sand causing an increase in bulk density, a decrease in total porosity and an increase in macroporosity and poultry manure causing a decrease in bulk density and an increase in macroporosity. While organic C content was increased more by biosolids than poultry manure the reverse was the case for soluble organic C, microbial biomass C and basal respiration. It was concluded that even after seawater neutralization, exchangeable and soluble Na, ESP and SAR in residue mud were very high and application of gypsum at least 5%, and subsequent leaching, will be required prior to revegetation.

Keywords: bauxite residue, red mud, revegetation, gypsum, organic amendments, leaching.

4.1 Introduction

Bauxite from far north Queensland is processed at two alumina refineries in northern Queensland, Australia. For every tonne of alumina produced during processing of bauxite, 1-2 tonnes of bauxite processing waste is also produced. This is deposited in land-based lagoons and impoundments surrounding the refinery. Bauxite residues have a high pH (11-13) and high salinity and sodicity (Jones and Haynes, 2011; Grafe et al., 2011) and the drainage from storage areas can pose an environmental risk and must be managed and treated for many decades after closure. For this reason, there is an increasing trend towards partial neutralization of residues prior to their deposition in storage areas (Grafe et al., 2011). At both the refineries, the alkaline mud is seawater neutralized prior to its deposition in the impoundments. Seawater neutralization was pioneered by the company and it results in the pH being reduced from 11-13 down to about 9.0 because soluble alkalinity is precipitated as poorly soluble Ca and Mg hydroxides and hydroxycarbonates (Hanahan et al., 2004; Palmer et al., 2009). Such neutralization not only alters pH but also reduces exchangeable Na percentage (by addition of Ca, Mg and K in the seawater) and it is also thought to influence the physical properties of the residues (Menzies et al., 2004; Hanahan et al., 2004).

As yet, there are only a few reports regarding the chemical, physical and microbial properties of seawater neutralized residues (Menzies et al., 2004, 2009; Hanahan et al., 2004) and, to date, there are no reports of its revegetation. Because the residue has already been partially neutralized it can be argued that there will be no need for *in situ* neutralization with gypsum prior to revegetation (A. Boullemant, personal communication, 2016) as is commonly carried out for un-neutralized mud. Nevertheless, leaching of the material will be essential in order to remove soluble salts (residual NaOH and seawater) prior to revegetation (Menzies et al., 2009). Limitations to revegetation will be similar, although less marked, to those for un-neutralized mud including salinity, sodicity, alkalinity, lack of microbial activity and a compact, fine-textured structure (Jones and Haynes, 2011). Gypsum might need to be applied in order to further neutralize the residue mud. In addition, other amendments may also be desirable including residue sand to improve physical conditions and organic matter (composts, manures) to increase microbial activity, nutrient supplying capacity and improve physical conditions.

In this study, the effects of amending seawater neutralized bauxite residue mud with residue sand (25% v/v), gypsum (1% w/v), poultry manure (6% w/v) and biosolids (6% w/v), followed by leaching, on soil chemical, physical and microbial properties was investigated. In a second experiment, the effects of 0, 1% and 5% gypsum application on chemical properties after leaching were studied.

4.2 Materials and Methods

4.2.1 Materials used

Residue mud and sand were separated and collected by hand sieving the residue slurry at the seawater neutralization plant situated at a refinery in north Queeensland immediately prior to deposition of residue into the disposal area. The mud was air-dried and crushed (< 2 mm) prior to use and the sand was air-dried. Biosolids were collected from the Oxley Creek Wastewater Treatment Plant (Brisbane). At this plant, the sewage sludge is treated by the Cambi process (155 ºC at 4.5 bar) and digested anaerobically prior to dewatering. Poultry manure was collected from a commercial egg producer. Organic materials were air-dried and ground/sieved (< 2 mm) prior to use. Gypsum was purchased from a local garden centre.

4.2.2 Experimental design

4.2.2.1 Experiment 1

There were 12 treatments consisting of (a) residue mud and (b) residue mud/residue sand (75:25) with addition of (i) control, (ii) poultry manure, (iii) biosolids, (iv) gypsum, (v) gypsum plus poultry manure and (vi) gypsum plus biosolids. The addition of 25% sand to the mud was chosen because it has been successfully used by a number of other workers (Jones and Haynes, 2011). Amendments were thoroughly mixed with the mud and mud/sand mixtures (1 L) and placed in 2 L plastic containers with mesh bottoms to allow drainage into polypropylene collecting containers. The mixtures were rewetted to 70% of water holding capacity. The pots were arranged in a randomized block design with 3 replicates and incubated at room temperature (24-30 ºC) for 4 weeks. Containers were opened and mixed each week to ensure adequate aeration. At the end of this period, samples were leached slowly over a 96-hour period with 6 pore volumes of distilled water. A previous study (Li et al., 2016) showed that after being leached with 6 pore volumes, greater than 95% of leachable ions had been removed from residue mud. Leachates were stored at 5 ºC until analysed. Following leaching the samples were incubated for a further four weeks. After incubation, samples were split into two subsamples. One was stored at 4 ºC for microbial and physical analysis and the other was air-dried and stored for chemical analysis.

4.2.2.2 Experiment 2

Because the effect of 1% gypsum on chemical properties did not show pronounced improvement a second experiment was set up including 3 treatments: control, 1% gypsum and 5% gypsum added to residue mud. The experimental procedure was identical to that of experiment 1. After incubation, leaching and final incubation, samples were air-dried and stored for chemical analysis.

4.2.3 Chemical analysis

EC and pH were analysed in a 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson, 1992). Exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) were extracted with 1M ammonium acetate (pH 7.0) (Rayment and Higginson, 1992) and analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Effective cation exchange capacity was calculated as the sum of exchangeable cations (Ca, Mg, K and Na). Exchangeable sodium percentage (ESP) was calculated as the percentage of exchangeable bases present as Na. Exchangeable Al was extracted with 1M KCl (1:10 ratio for 1 h) and Al analysed by ICP-AES. Saturated paste extracts were prepared (Rhoades, 1982) and extracted under vacuum. The pH and EC in extracts were measured using a glass electrode and Ca, Mg, K, Na and Al were analysed by ICP-AES. Extractable P was extracted with 0.5M $NaHCO_3$ (pH 8.5) (1:100 w/v ratio for 16 h) (Colwell, 1963) and measured colorimetrically by the molybdenum blue method method. Diethylenetriminepentaacetic acid (DTPA)-extractable metals were extracted according to Lindsay and Norvell (1978) (0.005M DTPA, 0.01M $CaCl_2$ and 0.1M TEA: 1:2 ratio for 2 h) and Zn, Cu, Mn, Fe, Pb, Cd and Cr were analysed by ICP-AES. Leachates were analysed for Al, Ca, K, Mg, Na, P (ICP-AES) and pH and EC using a pH/conductivity meter.

To determine their mineralogy, residues were subjected to X-ray diffraction analysis. Amorphous content was calculated by difference using a corundum internal standard of known amorphous content. The total content of P, K, Ca, Mg, Si, Fe, Al and Si in residue mud and sand was determined after microwave digestion using HF, HCl and HNO_3 and that in organic materials after nitric-perchloric acid digestion. Elemental content of extracts was determined by ICP-AES. Total C and N were measured by dry combustion method using a Carlo Erba C, H, N analyser (Rayment and Higginson, 1992). In order to calculate the organic C content of residues, inorganic C (HCO_3^-/CO_3-C) was removed from samples by treatment with 1M HCl to lower pH to 4.0 over a 4-day period (with intermittent vigorous mixing). Residual acid was neutralized by raising pH to 5.0 using 0.5M NaOH and the samples were dried at 50 ºC before analysis.

4.2.4 Microbial analysis

Microbial biomass C was estimated based on the difference between organic C extracted with 0.5M K_2SO_4 from chloroform-fumigated and unfumigated samples using a K_c factor of 0.45 (Wu et al., 1990). Soluble C in the K_2SO_4 extracts was analysed using a Shimadzu 5000A soluble C/N analyser. Values for the unfumigation samples were used as a measure of soluble C. Basal respiration was determined by placing 30 g oven-dry equivalent of moist compost in a 50 mL beaker and incubating the sample in the dark for 10 days at 25 ºC in a 1 L air tight jar along with 10 mL of 1M NaOH. The CO_2 evolved was determined by titration (Anderson, 1982). The metabolic quotient was calculated as basal respiration (mg CO_2-C per day) expressed per gram of biomass C.

4.2.5 Physical analysis

Bulk density was determined on naturally compacted samples (Haynes and Goh, 1977), particle density by the pycnometer method (Blake and Hartge, 1986) and total porosity by difference (Danielson and Sutherland, 1986). Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Pore size distribution was calculated as macropores (> 29 µm diameter, air-filled pores at -10 kPa), mesopores (0.2-29 µm diameter, drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter, water-filled pores at -1500 kPa). Field capacity was determined as the volumetric water content at -10 kPa and available water as that held between -10 and -1500 kPa.

4.2.6 Germination assay

A germination assay was carried out (in quadruplet) on residue treatments. 2 mL of aqueous extract (1/10 w/v) from composts was added to dishes (Belyaeva and Haynes, 2009). Ten seeds of watercress (*Lepidium sativum*) were placed on filter paper and dishes placed in the dark at 28 ºC. The germination percentages with respect to control (distilled water) and root lengths were determined after 5 days. The germination index (GI) was calculated as $GI = \%G \times Le/Lc$, where $\%G$ is the percentage of germinated seeds in each extract with respect to control, Le is the mean total root length of the germinated seeds in each extract, and Lc is the mean root length of the control (Belyaeva and Haynes, 2009). The control GI value is considered as 100%.

4.2.7 Statistical analysis

The statistical significance of experimental treatments was determined by subjecting the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test.

4.3 Results

4.3.1 Properties of the materials

The elemental content of residue mud and sand was dominated by Fe and there were also substantial amounts of Si, Al and Na present (Table 4.1). Residue sand had a greater content of Si and Fe than mud but the reverse was the case for Al, Ca, K, Mg, Na and P. The mineralogical content of mud and sand was 42 and 32% amorphous materials, 29 and 34% hematite, 11 and 9% sodalite, 6 and 8% boehmite, 2 and 4% goethite and 2 and 0.7% anatase respectively. Biosolids had a greater content of Fe, Al, Mg and P than poultry manure but the reverse was true for the Ca, K and Na content, pH and EC (Table 4.1).

4.3.2 Experiment 1

The cation content of leachates from all treatments was dominated by Na^+ and the anion content was dominated by Cl^- (Table 4.2). Addition of gypsum increased Na^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations in leachates. The ΣC exceeded the ΣA by a small amount for all leachates and ΣC–ΣA was greatest for the three sand-amended treatments where gypsum was not added (which also had the highest pH values of 8.5-8.7). Biosolids addition resulted in increased concentrations of Ca^{2+}, Mg^{2+}, K^+, Cl^- and SO_4^{2-} in leachates while poultry manure addition increased those of K^+ and Mg^{2+}. Addition of poultry manure, and particularly biosolids, increased $H_2PO_4^-$ concentrations in leachates. Concentrations of NH_4^+ were lowest in control and highest on biosolids treatments (Table 4.2). Concentrations of NO_3^- were less than 0.02 mmol L^{-1} in all treatments (data not shown). The EC was similar in all leachates but pH tended to be higher in the sand-amended treatments and lowered by gypsum application (Table 4.2).

Following leaching, the gypsum treatments had higher exchangeable Ca and K and lower exchangeable Na, ESP and pH compared to treatments where no gypsum had been added (Table 4.3). Gypsum had no significant effect on exchangeable Mg, Colwell P or EC. Addition of sand to mud reduced exchangeable Ca. Addition of poultry manure increased exchangeable Ca, Mg and K and Colwell P, tended to reduce ESP, but had no effect on exchangeable Na, ECEC, pH and EC. Addition

of biosolids increased exchangeable Ca and Mg, ECEC and Colwell P but decreased ESP and EC (Table 4.3).

Concentrations of Ca, Mg and K in saturation paste extracts were increased by gypsum addition whilst those of Na were decreased (Table 4.4). The SAR and pH were also decreased while EC was unaffected. Addition of sand to mud reduced concentrations of Na, Mg and K in saturation paste extracts, lowered SAR, tended to lower EC but had no effect on pH. Poultry manure addition increased concentrations of Ca, Mg, K and Na in paste extracts, lowered SAR and pH and increased EC. Addition of biosolids increased concentrations of Ca and Mg in extracts and lowered SAR (Table 4.4).

Gypsum addition had no measureable effect on physical conditions but addition of sand to mud increased bulk density, lowered total porosity and tended to increase macroporosity at the expense of mesoporosity (Table 4.5). It also lowered the amount of water held at field capacity. Addition of poultry manure lowered bulk density and increased macroporosity and tended to lower microporosity, available water and water held at field capacity. Addition of biosolids had little measureable effect on physical properties.

Neither addition of 25% sand nor gypsum had any measureable effect on organic C content or related soil microbial properties (Fig. 4.1). Organic C content of unamended residues was low (< 5.0 g kg^{-1}) and it was increased to 10-15 g kg^{-1} by addition of poultry manure and to 20-25 g kg^{-1} by biosolids addition. The C/N ratio decreased in the order control < poultry manure < biosolids while water soluble C was greater for the poultry manure than the other two main treatments. The addition of organic amendments had a greater effect on increasing basal respiration than microbial biomass but for both parameters values followed the order control < biosolids < poultry manure. The metabolic quotient was much greater for the organic-amended than control treatments.

Germination index was unaffected by additions of sand or gypsum but was greater in the poultry manure and biosolids than control treatments (Table 4.4).

4.3.3 Experiment 2

Increasing rates of applied gypsum increased concentrations of Ca^{2+}, Na^{+}, SO_4^{2-} and Cl^{-} present in leachates and as a consequence both ΣC and ΣA were increased (Table 4.6). Concentrations of Mg^{2+} and K^{+} in leachates also tended to increase, while those of $H_2PO_4^{-}$ and $Al(OH)_4^{-}$ were unaffected. The pH of leachates decreased while the EC increased.

Increasing rates of applied gypsum increased exchangeable Ca concentrations and decreased those of Na (Table 4.7). They also decreased ESP and pH and increased EC. The increase from 1% to 5% added gypsum caused a small decrease in pH from 9.3 to 9.0.

4.4 Discussion

Since the residues used had been treated with seawater they had an initial pH of 9.3 compared to 10-13 for un-neutralized residues (Grafe et al., 2011). Although the cationic composition of seawater is dominated by Na^+, it also contains significant quantities of other cations including Ca^{2+}, Mg^{2+} and K^+ (Rai et al., 2013). Partial neutralization of residues occurs because of precipitation of soluble alkalinity (HCO_3^-/CO_3^{2-}) as sparingly soluble Ca and Mg hydroxides and hydrocarbonates (particularly hydrocalcite) (Hanahan et al., 2004; Palmer et al., 2009). This is accompanied by a decrease in residue pH. Such precipitates were apparently present in amorphous, non-crystalline, forms since no such crystalline forms were detected by X-ray diffraction analysis.

Because seawater neutralization is routinely carried out in at the north Queensland refineries, and it has been suggested that field neutralization of the residue with gypsum may not be necessary prior to revegetation (A. Boullemant, personal communication, 2016). For that reason, a relatively low rate of gypsum of 1% was used in the first experiment as a comparison with no treatment (control). Nevertheless, during leaching, the pH of un-amended control residue rose from 9.3 back to 9.6. This increase in pH during leaching has been noted previously (Menzies et al., 2009; Li et al., 2016) and is attributable to dissolution of residual alkalinity present in the mud. The exact nature of this alkalinity is yet to be defined but may include precipitated amorphous hydrotalcite (from seawater neutralization) (Palmer et al., 2009) as well as sodalite and amorphous tricalcium aluminate hexahydrate (TCA) both formed during Bayer digestion (Menzies et al., 2009; Grafe et al., 2011). Sodalite was detected in substantial quantities in both mud and sand by X-ray diffraction and Menzies et al. (2009) attributed the increase in pH upon freshwater-leaching of seawater neutralized residue sand to dissolution of sodalite with the release of alkalinity and Na.

Another limitation of seawater neutralized residue in relation to its potential for revegetation is that although ESP had been lowered compared with non-neutralized material, Na^+ was still the predominant exchangeable and soluble cation present (ESP = 65-70%, SAR = 191). Such values are high since for soils ESP greater than 15% and SAR values above 13 are generally considered likely to reduce plant growth (Sumner, 1993). Thus, a reduction in the Na status of the residues is essential.

While the 1% gypsum addition maintained pH at 9.3 after leaching (compared with pH 9.6 for control), an addition of 5% lowered it to 9.0. This decrease in pH occurs because the added Ca^{2+} in the gypsum reacts with soluble alkalinity (HCO_3, CO_3^{2-}, $Al(OH)_4^-$ and OH^-) to form precipitates of calcite, tricalcium aluminate and hydrocalumite (Barrow, 1982). The addition of gypsum also increased exchangeable Ca, decreased exchangeable Na and lowered ESP after leaching. Indeed, in experiment 2, the decrease ESP for a 5% addition of gypsum was from 70% down to 48%. The reason for this is that added Ca^{2+} displaces Na^+ (and K^+ and Mg^{2+}) from cation exchange sites and the Na^+ then leaches with the added SO_4^{2-}. Because of the preponderance of Na in bauxite residues, reducing ESP to < 15% may not be practical but, in general, an ESP of < 40% is desirable in order to grow even saline/sodic-tolerant plants in residues (Haynes, 2015). Thus, addition of a rate of at least 5% gypsum, as is often applied to un-neutralized residue (Courtney and Timpson, 2005; Courtney et al., 2009), is desirable.

Addition of organic manures such as poultry manure or biosolids to improve nutrient supply and promote microbial activity had the added advantage of adding additional Ca^{2+} and Mg^{2+} to further displace exchangeable Na^+ which is then leached thus further lowering exchangeable Na and ESP. In the case of biosolids addition, the ECEC is increased (due to variable charge properties of the humic components present in the biosolids; see below) with the result that ESP was further reduced.

The major difference between the mud and sand was particle size although sand also had a higher Si and Fe and quartz content and a lower content of Al, Ca, K, Mg and Na. This difference was, however, small compared with that for some other bauxite deposits. For example, Jones et al. (2012), using residues from the Darling Range bauxite deposit in Western Australia, found residue sand had more than double the Si content of mud and 67% quartz content compared with only 17% for mud. In addition, the mud had a total and exchangeable Na content which was more than four times greater than that of the sand (Anderson, 2009; Jones et al., 2012). However, the bauxite deposit in north Queensland is one of the world's highest grade deposits (49-53% Al_2O_3) (Loughnan and Bayliss, 1961) and the larger particles have only a slightly greater Si and quartz content and lower Na content than the mud. As a result, addition of 25% sand to the mud had only a small effect on chemical properties of the medium lowering exchangeable Ca, Colwell P and EC. Thus although addition of sand to mud can sometimes cause significant reductions in exchangeable Na and ESP (Li et al., 2016), for the residues from north Queenlsand bauxite no such an effect was observed.

Since the residues had been seawater neutralized, the main ions present in leachates were Na^+ and Cl^- and as increasing rates of gypsum were added, increased concentrations of Ca^{2+}, and more particularly SO_4^{2-}, were present. That is, leaching initially removes the soluble salts present in solution (mainly

excess Na^+ and Cl^-) and this results in a large reduction in EC. For example, the initial EC of residue mud (1:5 extract) was 16.5 dS m^{-1} and this was reduced to 0.84 dS m^{-1} after leaching. The high P status of biosolids resulted in $H_2PO_4^-$ concentrations in leachates that were an order of magnitude greater than in control treatments. The P content of biosolids is characteristically high and in anaerobically digested sludges much of this is in soluble form (Haynes et al., 2009). A large accumulation of extractable P following land application of biosolids is common (Pierzynski, 1994; Hue, 1995) and the massive concentrations of extractable P encountered here in the biosolids treatments (> 1000 mg kg^{-1}) might well inhibit growth of some plants (Handreck and Black, 2002). Even though bauxite residue is composed primarily of Fe oxides, and therefore has a high phosphate adsorption capacity (Huang et al., 2008), the massive amount of soluble P present meant that significant amounts of P were not retained but rather leached. Poultry manure also has a characteristically high P status (Smith et al., 2004) and in the poultry manure treatments Colwell P levels were raised to between 450 and 560 mg kg^{-1} and leachate $H_2PO_4^-$ concentrations were raised to above those of control treatments.

Both biosolids and poultry manure are known to accumulate NH_4^+ (Nahm, 2003; Haynes et al., 2009) and, as a consequence, NH_4^+ concentrations in leachates were elevated by an order of magnitude above those in controls by addition of both amendments. The lack of NO_3^- in leachates from these two treatments confirms earlier work (Jones et al., 2015) that nitrification can be very slow in bauxite residues. In general, nitrification tends to be slow in freshly deposited residue sand (Chen et al., 2010) but occurs more readily with time after leaching and plant establishment (Goloran et al., 2013).

In general, the effects of amendments on physical properties were small. Courtney and Timpson (2005) and Courtney et al. (2009) suggested that addition of 25% sand to mud generated greater permeability, aeration, drainage and root penetration and results presented here did demonstrate an increase in macroporosity even though total porosity was decreased. It is likely that the fine nature of mud particles means they can fill some of the voids between larger sand particles thus reducing total porosity. Similarly, addition of biosolids, which is composed of finely divided particles, had little effect on physical properties. By contrast, addition of the coarse-textured poultry manure caused a decrease in bulk density and an increase in macroporosity. The very low macroporosity in mud characteristically results in surface layers of mud becoming waterlogged during wet periods of the year (Jones and Haynes, 2011). The increase in macroporosity with a combination of sand and poultry manure additions from less than 6% to 19-21% is therefore of practical significance.

Xue et al. (2016) suggested that gypsum additions to residues would reduce dispersion (by replacement of Na^+ by Ca^{2+}) and increase aggregation thus improving physical properties (as occurs

in soils) but our results showed that additions of gypsum had no effect on total porosity of pore size distribution. This difference probably arises because of the presence of pozzolanic agents in residue mud (Liu and Zhang, 2011). Because of these agents, when the mud is dried it solidifies and the particles formed by crushing and sieving are relatively strongly bound together and not subject to Na^+-induced dispersion.

Residue mud is an inorganic material that has been treated with both chemicals (NaOH) and heat and this effectively sterilizes it so that it harbours a very small and inactive microbial community. While colonization of newly exposed parent material by soil microorganisms is rapid mainly through aeolian transport of bacterial cells and fungal spores (Haynes, 2014), microbial growth and activity in residues is greatly limited by low C and N availability. As a result, during the initial stages of community assembly, heterotrophic microflora exist predominantly in resting stages. For example, Banning et al. (2011) found that bacterial and fungal communities developed rapidly on bauxite residue sand and diversity was similar to that under a coastal sand dune ecosystem after only 0.5 years of rehabilitation. Nevertheless, the size of the microbial biomass was very much smaller in the bauxite residue due to the low organic matter accumulation. The most practicable and effective way of increasing microbial activity in residues is to add organic matter (Jones and Haynes, 2011; Haynes 2015).

As expected, addition of biosolids and poultry manure increased organic C content greatly and the size (microbial biomass C) and activity (basal respiration) of the soil microbial community were also greatly increased. While organic C was increased more by addition of biosolids than poultry manure, the concentration of water soluble C and N were increased much more dramatically by poultry manure. This reflects the fact that during waste water treatment the organic matter in biosolids undergoes decomposition, stabilization and humification (Haynes et al., 2009). By contrast, freshly deposited poultry manure was collected directly from a poultry farm so it contained much higher concentrations of easily decomposable soluble C and N than biosolids. As a result, both microbial biomass and basal respiration were increased more by addition of poultry manure than biosolids. The large increase in metabolic quotient induced by additions of poultry manure and biosolids reflects the addition of a copious supply of available C, and thus intense microbial activity (and CO_2 evolution) rather than microbial stress (Sparling, 1997). The C/N ratio was also greatly reduced by organic matter additions. This is because the small amount of organic C content of residue mud is composed mainly of Na oxalate and has an insignificant N content. The oxalate is formed during caustic degradation of humic material which is introduced as a contaminant with the bauxite ore (Jones and Haynes, 2011).

4.5 Conclusions

Even after seawater neutralization the values for exchangeable Na, ESP and SAR in residue mud are very high and need to be reduced prior to revegetation. Although the pH was lowered to 9.3 by seawater neutralization, after leaching it rose to 9.6. Such results suggest that at least 5% gypsum addition will be needed to displace exchangeable Na (which then can be leached) and arrest the pH increase that occurs during leaching. Addition of organic wastes (biosolids, poultry manure) is an effective way of increasing microbial activity in residues as well as adding nutrients and aiding in acidification.

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Table 4.1 *pH, EC and elemental composition (g kg^{-1}) of the source materials.*

Material	pH	EC (dS m^{-1})	Si	Fe	Al	Ca	K	Mg	Na	P
Residue mud	9.3	16.5	74	199	64	7.8	1.5	3.5	79.6	0.40
Residue sand	9.3	7.5	101	247	55	2.2	1.1	1.5	57.1	0.31
Biosolids	7.2	4.1	N/A*	18.6	12.9	27.5	4.3	16.7	0.96	46.5
Poultry manure	7.9	5.8	N/A	2.1	3.3	82.7	17.9	6.5	4.4	17.9

*N/A = not analysed

Table 4.2 *Effect of addition of 25% residue sand, gypsum (G), poultry manure (PM) and biosolids (BS) to bauxite residue mud on mean ionic composition of leachates (mmol$_c$ L^{-1}).*

Ion	Mud						25% sand					
	Control	PM	BS	Control(G)	PM(G)	BS(G)	Control	PM	BS	Control(G)	PM(G)	BS(G)
Ca^{2+}	1.7^{b}	1.8^{b}	3.3^{c}	6.5^{e}	4.6^{d}	7.2^{e}	0.7^{a}	1.0^{ab}	1.5^{b}	2.9^{c}	2.9^{c}	4.8^{d}
K^{+}	1.6^{a}	3.5^{c}	2.2^{ab}	1.8^{a}	3.7^{c}	2.6^{b}	1.4^{a}	3.6^{c}	2.0^{ab}	1.7^{a}	3.7^{c}	2.6^{b}
Mg^{2+}	1.8^{ab}	2.0^{ab}	2.7^{b}	3.1^{b}	3.6^{c}	4.4^{c}	1.2^{a}	1.4^{a}	1.4^{a}	2.3^{ab}	2.9^{b}	3.0^{b}
Na^{+}	141^{a}	145^{a}	153^{b}	158^{b}	156^{b}	174^{c}	142^{a}	149^{a}	156^{b}	146^{a}	160^{bc}	175^{c}
NH_4^{+}	0.11^{a}	1.0^{b}	1.4^{c}	0.12^{a}	1.2^{c}	1.5^{c}	0.16^{a}	1.3^{b}	1.5^{c}	0.19^{a}	1.3^{b}	1.5^{c}
ΣC	146^{a}	153^{a}	163^{b}	169^{b}	169^{b}	190^{c}	145^{a}	156^{ab}	162^{b}	153^{ab}	171^{b}	187^{bc}
Cl^{-}	108^{a}	102^{a}	114^{b}	120^{c}	112^{b}	128^{c}	0.4^{a}	106^{a}	110^{ab}	101^{a}	116^{b}	122^{c}
SO_4^{2-}	27.9^{b}	28.1^{b}	33.6^{bc}	41.9^{c}	40.4^{c}	49.8^{d}	17.2^{a}	17.7^{a}	18.1^{a}	42.6^{c}	44.2^{cd}	49.9^{d}
$H_2PO_4^{-}$	0.01^{a}	0.06^{b}	0.23^{c}	0.01^{a}	0.06^{b}	0.23^{c}	0.01^{a}	0.11^{b}	0.29^{d}	0.01^{a}	0.09^{b}	0.22^{c}
$Al(OH)_4^{-}$	0.15^{bc}	0.18^{c}	0.16^{c}	0.05^{a}	0.12^{b}	0.10^{b}	0.51^{e}	0.33^{d}	0.34^{d}	0.02^{a}	0.02^{a}	0.02^{a}
ΣA	136^{ab}	130^{a}	148^{b}	162^{c}	152^{b}	178^{d}	122^{a}	124^{a}	129^{a}	144^{b}	160^{c}	172^{d}
ΣC- ΣA	10^{a}	23^{ab}	15^{a}	7^{a}	17^{ab}	12^{a}	20^{ab}	25^{ab}	33^{b}	9^{a}	11^{a}	15^{a}
pH	8.1^{b}	8.1^{b}	8.1^{b}	7.7^{a}	8.0^{b}	8.0^{b}	8.7^{c}	8.5^{bc}	8.5^{bc}	8.2^{b}	8.1^{b}	8.2^{b}
EC(dS m^{-1})	36^{a}	37^{a}	39^{a}	40^{a}	41^{a}	41^{a}	36^{a}	38^{a}	38^{a}	37^{a}	38^{a}	38^{a}

Means within one row followed by the same letter are not significantly different at $P \leq 0.05$.

Table 4.3 *Effect of addition of 25% residue sand, gypsum (G), poultry manure (PM) and biosolids (BS) to bauxite residue mud on exchangeable cations, effective cation exchange capacity (ECEC), exchangeable sodium percentage (ESP), Colwell-extractable P, pH and electrical conductivity (EC).*

Treatment		Exchangeable cations ($cmol_c\ kg^{-1}$)				ECEC ($cmol_c\ kg^{-1}$)	ESP (%)	Colwell P ($mg\ kg^{-1}$)	pH	EC ($dS\ m^{-1}$)
		Ca	Mg	K	Na					
Mud	Control	6.4^{a}	3.2^{ab}	0.22^{b}	27.0^{c}	42.1^{a}	64^{c}	9.9^{a}	9.6^{b}	0.84^{b}
	PM	8.5^{b}	3.5^{ab}	0.30^{c}	26.3^{b}	44.3^{a}	57^{b}	229.0^{b}	9.5^{b}	0.83^{b}
	BS	11.1^{d}	3.9^{b}	0.25^{b}	26.5^{b}	51.1^{c}	53^{a}	670.2^{c}	9.5^{b}	0.77^{a}
	Control(G)	6.7^{ab}	3.3^{ab}	0.22^{b}	25.3^{b}	42.8^{a}	59^{b}	9.4^{a}	9.3^{a}	0.86^{b}
	PM(G)	9.5^{c}	3.6^{b}	0.25^{b}	24.9^{a}	50.1^{c}	54^{a}	217.4^{b}	9.2^{a}	0.85^{b}
	BS(G)	12.6^{d}	3.8^{b}	0.29^{c}	24.9^{a}	54.1^{c}	48^{a}	661.1^{c}	9.3^{a}	0.77^{a}
25% sand	Control	5.8^{a}	2.6^{a}	0.15^{a}	28.0^{c}	42.3^{a}	69^{d}	7.2^{a}	9.6^{b}	0.79^{ab}
	PM	7.7^{b}	3.0^{a}	0.20^{ab}	25.5^{b}	42.7^{a}	63^{c}	266.8^{b}	9.5^{b}	0.75^{a}
	BS	9.5^{c}	3.1^{a}	0.12^{a}	25.0^{b}	46.3^{b}	60^{c}	746.8^{c}	9.5^{b}	0.73^{a}
	Control(G)	6.7^{ab}	2.7^{a}	0.19^{ab}	26.8^{b}	42.2^{a}	64^{c}	6.1^{a}	9.3^{a}	0.76^{a}
	PM(G)	9.0^{c}	3.1^{a}	0.18^{ab}	24.4^{a}	45.4^{b}	58^{b}	226.1^{b}	9.2^{a}	0.76^{a}
	BS(G)	11.3^{d}	3.3^{ab}	0.16^{a}	24.3^{a}	47.8^{b}	54^{a}	717.7^{c}	9.2^{a}	0.73^{a}

Means within a column followed by the same letter in a column are not significantly different at $P \leq 0.05$.

Table 4.4 *Effect of addition of 25% residue sand, gypsum (G), poultry manure (PM) and biosolids (BS) to bauxite residue mud on Ca, Mg, K and Na content in saturation paste extracts ($mmol_c\ kg^{-1}$), sodium absorption ratio (SAR), effective cation exchange capacity (ECEC), pH and electrical conductivity (EC) in saturation paste extracts and on germination index.*

Treatment		Ca	Mg	K	Na	SAR	pH	EC ($dS\ m^{-1}$)	Germination index (%)
Mud	Control	0.02^{a}	0.31^{ab}	0.81^{b}	77.9^{b}	191^{e}	9.1^{b}	2.6^{b}	58^{ab}
	PM	0.07^{b}	1.71^{d}	1.53^{d}	102.3^{d}	108^{d}	8.2^{a}	2.9^{b}	69^{c}
	BS	1.10^{d}	1.66^{d}	0.83^{b}	77.4^{b}	66^{b}	9.0^{b}	2.4^{b}	67^{c}
	Control(G)	0.31^{c}	0.50^{b}	1.11^{c}	70.3^{b}	110^{d}	8.9^{b}	2.8^{b}	56^{a}
	PM(G)	0.93^{d}	2.14^{e}	1.69^{de}	93.8^{d}	76^{b}	8.0^{a}	3.2^{b}	64^{b}
	BS(G)	1.68^{e}	1.13^{c}	1.01^{c}	71.6^{b}	60^{ab}	8.9^{b}	2.6^{b}	68^{c}
25% sand	Control	0.02^{a}	0.21^{a}	0.73^{a}	58.7^{a}	173^{e}	9.3^{b}	2.2^{a}	54^{a}
	PM	0.09^{b}	1.16^{c}	1.47^{d}	82.1^{c}	104^{d}	9.0^{b}	2.3^{a}	75^{c}
	BS	1.16^{d}	0.91^{c}	0.96^{c}	76.3^{b}	74^{b}	9.1^{b}	2.4^{a}	72^{c}
	Control(G)	0.33^{c}	0.43^{b}	0.77^{ab}	55.7^{a}	90^{c}	9.2^{b}	2.1^{a}	53^{a}
	PM(G)	1.10^{d}	1.71^{d}	1.83^{e}	73.9^{b}	62^{ab}	8.9^{b}	2.7^{b}	64^{b}
	BS(G)	1.81^{e}	1.70^{d}	1.15^{c}	70.4^{b}	51^{a}	9.0^{b}	2.4^{a}	62^{b}

Means within a column followed by the same letter in a column are not significantly different at $P \leq 0.05$.

Table 4.5 *Effect of addition of 25% residue sand, gypsum (G), poultry manure (PM) and biosolids (BS) to bauxite residue mud on bulk density, total porosity, pore size distribution, available water and field capacity.*

Treatment		Bulk density (mg m^{-3})	Total porosity (m^3 m^{-3})	Pore size distribution (%)			Available Water (kg m^{-3})	Field Capacity (kg m^{-3})
				Micropores (<0.20 µm)	Mesopores (0.20-29 µm)	Macropores (>29 µm)		
Mud	Control	0.89^{b}	0.69^{b}	42^{b}	54^{b}	4^{a}	370^{c}	655^{c}
	PM	0.80^{a}	0.71^{b}	37^{ab}	46^{ab}	17^{b}	328^{b}	592^{bc}
	BS	0.92^{b}	0.66^{ab}	40^{b}	60^{c}	0^{a}	411^{d}	718^{d}
	Control(G)	0.88^{b}	0.69^{b}	44^{b}	50^{b}	6^{a}	347^{b}	637^{c}
	PM(G)	0.81^{a}	0.70^{b}	34^{a}	53^{b}	13^{b}	377^{c}	624^{c}
	BS(G)	0.85^{ab}	0.68^{b}	44^{b}	54^{b}	2^{a}	373^{c}	657^{c}
25% sand	Control	1.02^{c}	0.65^{a}	40^{b}	47^{ab}	13^{b}	309^{a}	568^{b}
	PM	0.92^{b}	0.67^{ab}	38^{ab}	41^{a}	21^{c}	277^{a}	513^{a}
	BS	0.98^{c}	0.64^{a}	41^{b}	56^{c}	3^{a}	362^{c}	622^{c}
	Control(G)	1.00^{c}	0.66^{ab}	43^{b}	42^{a}	15^{b}	273^{a}	544^{b}
	PM(G)	0.92^{b}	0.68^{b}	35^{a}	46^{ab}	19^{bc}	312^{a}	528^{ab}
	BS(G)	0.97^{c}	0.65^{a}	42^{b}	49^{b}	9^{ab}	319^{ab}	583^{b}

Means within a column followed by the same letter in a column are not significantly different at $P \leq 0.05$.

Table 4.6 *Effect of increasing rates of gypsum addition on mean ionic composition of leachates (mmol$_c$ L^{-1}) in experiment 2.*

Ion	Control	Gypsum (1%)	Gypsum (5%)
Ca^{2+}	1.7^a	8.2^b	32.9^c
K^+	1.4^a	1.6^{ab}	1.9^b
Mg^{2+}	1.5^a	2.8^b	3.1^b
Na^+	126^a	184^b	256^c
ΣC	131^a	197^b	294^c
Cl^-	95.5^a	138^b	193^c
SO_4^{2-}	26.6^a	40.9^b	88.6^c
$H_2PO_4^-$	0.01^a	0.02^a	0.02^a
$Al(OH)_4^-$	0.13^a	0.15^a	0.16^a
ΣA	122^a	179^b	282^c
ΣC- ΣA	9^a	18^a	12^a
pH	8.3^b	8.0^{ab}	7.5^a
EC(dS m^{-1})	30^a	44^b	49^c

Means within one row followed by the same letter are not significantly different at $P \leq 0.05$.

Table 4.7 *Effect of increasing rates of gypsum addition to bauxite residue mud on exchangeable cations, ECEC, ESP, pH and EC*

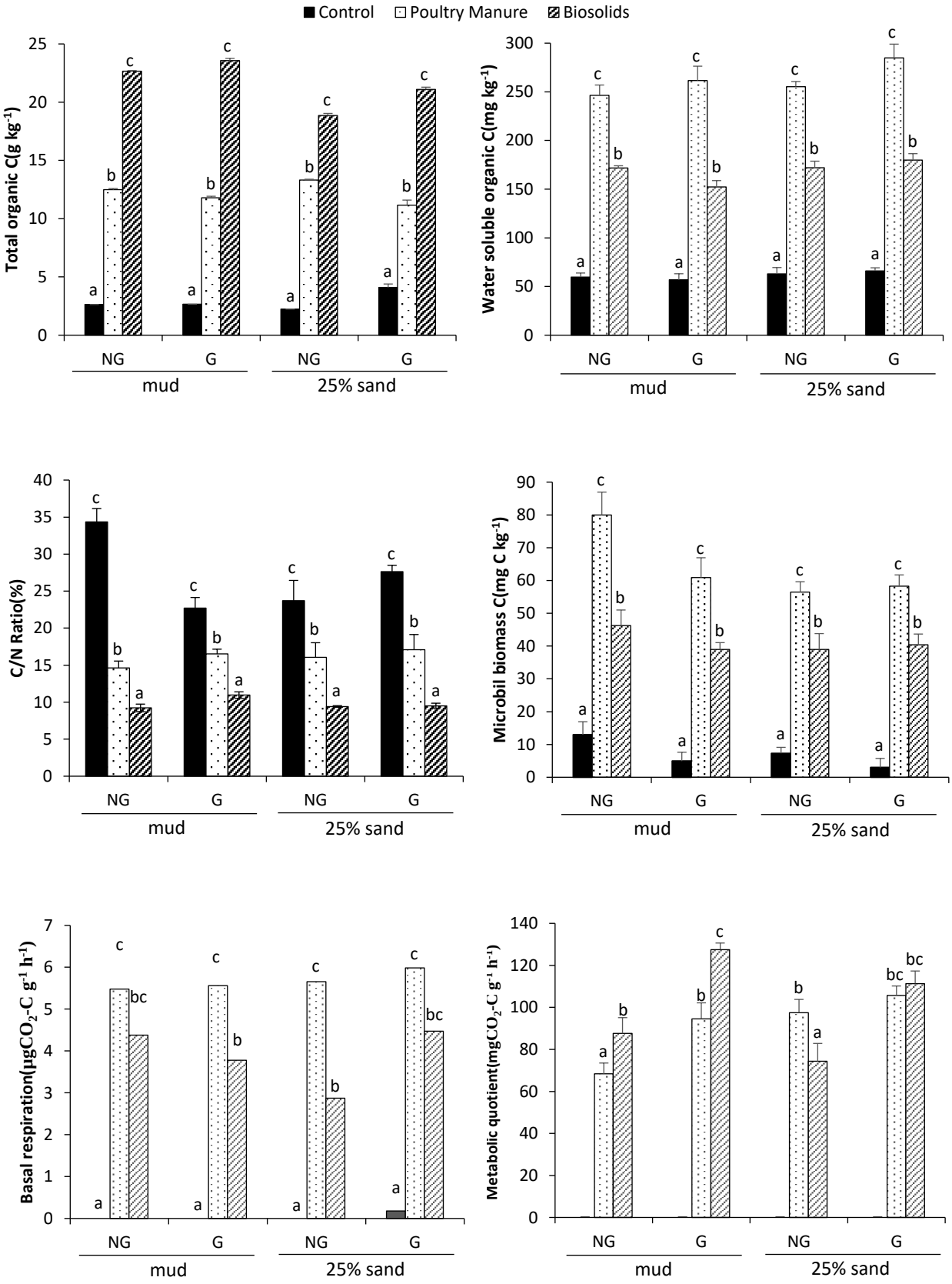
Treatments	Exchangeable cations ($cmol_c\ kg^{-1}$)				ECEC ($cmol_c\ kg^{-1}$)	ESP (%)	pH	EC ($dS\ m^{-1}$)
	Ca	Mg	K	Na				
Control	6.3^a	3.2^b	0.22^a	27.2^c	40.8^b	64.2^b	9.7^c	0.84^a
Gypsum (1%)	6.9^a	3.3^b	0.22^a	25.3^b	41.4^b	61.1^b	9.3^b	0.86^a
Gypsum (5%)	14.4^b	2.7^a	0.24^a	13.6^a	36.3^a	37.5^a	9.0^a	3.02^b

Means within a column followed by the same letter in a column are not significantly different at $p \leq 0.05$.

Figure Captions

Fig. 4.1. Effect of addition of 25% residue sand, gypsum (G), poultry manure and biosolids to bauxite residue mud on total organic C, soluble C, C/N ratio, microbial biomass, basal respiration and metabolic quotient. Means followed by same letters are not significantly different at $P \leq 0.05$.

Fig. 4.1


Control
Poultry Manure
Biosolids
Total organic C(g kg-1)
Water soluble organic C(mg kg-1)
C/N Ratio(%)
Microbil biomass C(mg C kg-1)
Basal respiration(µgCO2-C g-1 h-1)
Metabolic quotient(mgCO2-C g-1 h-1)
NG
G
mud
25% sand

5. Some physical properties of seawater neutralized bauxite residue and the effect of addition of amendments and leaching on chemical and microbial properties and plant growth

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Abstract: Laboratory and greenhouse experiments were carried out to evaluate the effects of drying and rewetting on the physical properties of seawater-neutralized bauxite residue, the effects of addition of organic amendments (biosolids and cattle manure), gypsum and subsequent leaching on improving the properties of residue as growth medium for Rhodes grass (*Chloris gayana*). Bauxite residue mud was observed to lose considerable volume and form a solid massive structure when dried for the first time. When this material was crushed and sieved, the 1-2 and 2-5 mm diameter aggregates were found to be highly water stable as estimated by wet sieving. When the previously dried < 2 mm fraction was rewetted, mixed to form a paste and then re-dried, it did not form water stable aggregates of diameter > 2 mm. Additions of organic amendments had no measurable effect on the pore size distribution of a growth medium formed from previously dried mud sieved to produce 2-5 mm aggregates. Leaching of the mud caused a rise in pH in control treatments from 9.1 to 10.1 when measured in water and from 8.5 to 9.6 when measured in saturation paste extracts. The pH in saturation paste extracts was lowered by additions of gypsum, cattle manure and biosolids both before and after leaching and the addition of gypsum, gypsum plus organic manures and biosolids-alone all prevented the pH from rising, during leaching, to values above those recorded in the unleached control. In amended treatments, yields of Rhodes grass were greatly promoted by leaching (due to reductions in soluble Na, SAR and EC) and were greatest in the leached biosolids and biosolids plus gypsum treatments.

Keywords: bauxite residue, red mud, revegetation, gypsum, organic amendments, leaching.

5.1 Introduction

Bauxite is refined by the Bayer process and for every tonne of alumina produced, 1-2 tonnes of alkaline, saline, bauxite processing residue (red mud) is produced (Hind et al., 1999; Kumar et al., 2006). This material is typically deposited in land-based impoundments surrounding the refinery. Drainage of alkaline leachate from residue storage areas is an environmental concern and must be managed for many decades after closure of the refinery. In addition, revegetation of the storage area is a key closure strategy for the refinery. Revegetation is usually carried out (after addition of amendments such as gypsum and organic manures) using plants known to be tolerant to salinity/sodicity (Jones and Haynes, 2011; Xue et al., 2016).

At the two alumina refineries in north Queensland, alkaline bauxite residue is seawater neutralized prior to deposition in the storage areas. During seawater neutralization, the pH is lowered from 11-13 down to about 9.0 because soluble alkalinity is precipitated as poorly soluble Ca and Mg hydroxides and hydroxycarbonates and sodicity is reduced by addition of Ca, Mg and K in the seawater (Hannahan et al., 2004; Menzies et al., 2004). This technology is now used at other refineries around the world and has been promoted as an effective method of converting residue into a relatively benign material (Hanahan et al., 2004).

At present there are no reports on revegetation of seawater neutralized residue mud or what steps are necessary to amend the residue prior to revegetation. However, in previous studies carried out at this laboratory (Chapters 3 and 4) it has been shown that although the ESP of residues is reduced by seawater neutralization, the salinity is raised appreciably to levels which are potentially unsuitable for growth of the vast majority of land plants. Leaching will therefore be necessary in order to move soluble salts out of the profile before revegetation is undertaken. However, leaching was also shown to result in an increase in residue pH from about 9 back up to about 10 due to dissolution of residual alkalinity present in the residue. Whilst it had been postulated that gypsum applications would not be necessary prior to revegetation of seawater neutralized residue (due to the previous precipitation of soluble alkalinity) results showed that even a low rate of gypsum application (e.g. 1%) was not sufficient to alleviate the increase in pH that occurred during leaching and that an application of 5% gypsum was more appropriate.

Growth of plants in residue mud can be limited by its unsuitable physical properties since newly deposited mud forms a paste that waterlogs easily while after drying the mud forms a massive solid structure (Wehr et al., 2006). Nonetheless, under field conditions, following tillage, a tilth suitable for seedling germination and growth can be formed (Courtney et al., 2009; Aluminium for Future

Generations, 2016). The reason for this is unclear and management of physical properties, particularly after drying, deserves further investigation.

In this study, we investigated (1) the effects of drying and rewetting on the physical properties of seawater-neutralized residue, (2) the extent to which leaching is necessary prior to revegetation, (3) the effectiveness of amendments (gypsum, cattle manure and/or biosolids) in improving the properties of residue as a growth medium and (4) the growth of the saline tolerant Rhodes grass *(Chloris gayana)* in the leached and amended treatments.

5.2 Materials and Methods

5.2.1 Materials

Residue mud as it was deposited in storage areas (i.e. 97% mud, 3% sand) was collected from an alumina refinery in north Queensland. Samples were collected immediately after seawater neutralisation and were then air-dried and crushed (< 5 mm). The 2-5 mm fraction was used in the main experiment. Gypsum and cattle manure were purchased from a local garden centre. Biosolids were collected from the Oxley Creek Wastewater Treatment Plant (Brisbane). They had been treated by Cambi process (155 °C at 4.5 bar) and digested anaerobically prior to dewatering. Amendments were all air-dried, ground and sieved (< 2 mm) prior to use.

5.2.2 Greenhouse study

A bulk sample of 2-5 mm diameter aggregates was leached with one pore volume of water to remove excess, easily removed, salts. This was done because previous results had shown that without any leaching, the seawater neutralized material is unlikely to support plant growth. There were 6 main treatments consisting of (a) control, (b) gypsum (5% v/v), (c) cattle manure (6% w/v), (d) biosolids (6% w/v), (e) gypsum with cattle manure and (f) gypsum with biosolids which were replicated 12 times. Amendments were thoroughly mixed with dried mud samples (1.5 L of 2-5 mm diameter aggregates), placed in 2 L plastic pots and rewetted to 70% water holding capacity. The pots were arranged in a randomized block design and incubated for 6 weeks in a glasshouse. The glasshouse had an air temperature of 24 to 28 °C. At the end of this period, 6 replicates were leached with 6 pore volumes of water (designated as “leached”) and the other 6 replicates were not leached (designated as “unleached”). This resulted in an experiment having 12 treatments and 6 replicates. Pots were left to dry to 70% water holding capacity over a two-week period. Three replicate pots of each treatment

were removed and then split into two subsamples. One was stored at 4 °C for microbial and physical analysis and the other was air dried and stored for chemical analysis.

Thirty seeds of Rhodes grass (*Chloris gayana* Kunth cv. Katambora) were sown in each of the other three replicates of each treatment and after 10 days seedlings were thinned to 15 per pot. Plant tops were harvested at 8, 14 and 20 weeks after sowing. At the beginning of the experiment, and after 8 and 14 weeks, a basal dressing of N (NH_4NO_3), P ($Ca(H_2PO_4)$, K (K_2SO_4), Mg ($MgSO_4$), Mo ($NH_4Mo_7O_{24}$), Zn ($ZnSO_4$), Mn ($MnSO_4$), Cu ($CuSO_4$) and B (H_3BO_3) of 220, 25, 200, 100, 10, 10 10, 10, 10 and 4 mg kg^{-1} respectively was applied to each pot. After 20 weeks, roots were carefully separated from the pots and washed free of adhering mud. Above-ground herbage was oven dried (70 °C), weighed and ground (< 1 mm) for subsequent elemental analysis.

5.2.3 Physical analysis

Bulk density was measured on naturally compacted field moist samples (formed from 2-5 mm aggregates) at 70% water content (Haynes and Goh, 1978), particle density by the pycnometer method (Blake and Hartge, 1986) and total porosity by the difference (Danielson and Sutherland, 1986). Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Pore size distribution was calculated as macropores (> 29 µm diameter, air-filled pores at -10 kPa), mesopores (0.2-29 µm diameter, drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter, water-filled pores at -1500 kPa). Field capacity was determined as the volumetric water content at -10 kPa and available water as that held between -10 and -1500 kPa.

A number of experiments were carried out to study the effects of drying on the physical properties of mud. The volume of a sample of freshly deposited "wet" mud paste (60% water content) of known mass was measured by displacement using oven-dried, fine silica sand (< 1 mm diameter; of known density) as a displacing agent. Wet samples of known mass were then dried at 70 ºC until there was no further loss of mass. The volume of the dried samples was then measured by displacement as described above. Dried samples were then placed in beakers filled with deionised water and left for 5 days. The samples were then removed, surface water removed with a tissue and the volume measured again as described above.

The wet sieving technique was used to investigate the stability of dried mud aggregates. Air-dried residue was crushed and sieved and two size classes: 2-5 and 5-10 mm diameter were collected. Aggregate stability of each group was determined by wet sieving (Haynes, 1993). For the 5-10 mm fraction, a sample (15 g) was transferred to the upper set of 2 sieves having 5 and 2 mm diameter

apertures. The water level was maintained to ensure the upper sieve was just submerged at the highest point of oscillation. The oscillation rate was 40 cycles per minute, the amplitude of sieving was 20 mm and the period of sieving was 15 min. The mass of residue remaining on the 5 and 2 mm sieves was measured after oven drying. For the 2-5 mm fraction, the sieve sizes used were 2 and 1mm. To determine whether dried mud in fine fractions could bind together to form a massive structure again after rewetting (and then subsequent drying), air-dried residue (< 2 mm) was mixed with gypsum (5% w/v), cattle manure (6% w/v), biosolids (6% w/v) or nothing (control), rewetted to form a paste (50% water content) and incubated for 14 days at room temperature (24 to 28 °C). The material was then air-dried and dry-sieved using a 2 mm sieve. The stability of the > 2 mm fraction was estimated by wet sieving, as described above, using 2 and 1 mm sieves.

5.2.4 Chemical analysis

EC and pH of samples were measured in 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson, 1992). Exchangeable bases (Ca, K, Na, and Mg) were extracted with 1M ammonium acetate (pH 7) (Rayment and Higginson, 1992) and analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable cations (Ca, Mg, K and Na) (after subtraction of the cations in saturated paste extracts from the ammonium acetate-extractable values) Exchangeable sodium percentage (ESP) was calculated (using the same values) as the percentage of exchangeable bases present as Na. Saturated paste extracts were prepared (Rhoades, 1982) and extracted under vacuum. The EC, pH, Al, Ca, K, Na and Mg in the extracts were measured as outlined above. Bicarbonate-extractable P was extracted with 0.5M $NaHCO_3$ (pH 8.5) (1:100 w/v for 16 h) (Colwell, 1963) and measured colorimetrically by the molybdenum blue method. Total organic C and N content of residue were measured by dry combustion using a Carlo Erba C, H, N analyser (Rayment and Higginson, 1992).

Plant samples were digested on an open-block with a starting and finishing temperature of 110 and 250 °C in nitric-perchloric acid (5:1 v/v ratio) (Martinie and Schilte, 1976) and the total content of Al, B, Ca, Cd, Cr, Fe, K, Na, Mg in the extracts was analysed by ICP-AES while P was determined colorimetrically. Total N in samples was measured as described above for residue.

5.2.5 Microbial analysis

Microbial biomass C was calculated based on the difference between organic C extracted with 0.5M K_2SO_4 from chloroform-fumigated and unfumigated samples using a K_c factor of 0.45 (Wu et al., 1990). Soluble C in the K_2SO_4 extracts was analysed using a Shimadzu 5000A soluble C/N analyser. Basal respiration was determined by placing 30 g oven-dry equivalent of most samples in a 50 mL beaker and incubating the sample in the dark for five days at 25 °C in a 2 L air-tight jar with 10 mL of 1M NaOH. The CO_2 evolved was determined by titration (Anderson, 1982). The metabolic quotient was calculated as basal respiration (mg CO_2-C g^{-1} h^{-1}) expressed per gram of biomass C.

5.2.6 Statistical analysis

The statistical significance of experimental treatments was determined by subjecting the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test. The relationships between cumulative shoot mass, root mass and total dry matter and various measures of salinity and sodicity in the treatments were fitted to linear, quadratic and cubic regression functions. Since quadratic and cubic functions did not show better fits, linear fits are reported below.

5.3 Results

5.3.1 Properties of the source materials

The major elemental component of the bauxite residue was Fe and there were also substantial amounts of Si, Al and Na present (Table 5.1). Biosolids contained substantial amounts of Ca, Mg, Fe and Al while the major components of cattle manure were Fe, Ca and Al. The P content of biosolids was much greater than that for the other materials. The pH of the residue mud, biosolids and cattle manure was 9.2, 7.0 and 6.9 respectively (data not shown).

5.3.2 Chemical properties

The major exchangeable (ammonium acetate-extractable) cation present in both unleached and leached samples was Na (Table 5.2). Leaching caused a decrease in exchangeable Ca, Mg, K as well as Na. Addition of biosolids, cattle manure and gypsum all increased exchangeable Ca, Mg and K levels. Exchangeable Al concentrations were decreased by additions of amendments and the effect was more significant following leaching. While EC was decreased for about 60% by leaching, pH

was raised except where gypsum had been applied (Table 5.2). Addition of gypsum, cattle manure and biosolids all tended to lower pH substantially. The corrected ECEC ranged from 18-23 $cmol_c\ kg^{-1}$ and was not significantly affected by addition of amendments or leaching. Values for ESP were lowered by addition of amendments. Largest reductions occurred where gypsum either alone or in combination with organic amendments had been added (Table 5.2) and for amended treatments, values tended to be decreased by leaching. Colwell-extractable P was increased by additions of cattle manure and more particularly biosolids but not significantly affected by leaching (Table 5.3).

The pH in saturation paste extracts was lowered by additions of amendments and leaching caused an increase in pH where gypsum had not been applied (Table 5.3). The EC was significantly reduced by leaching and increased by additions of amendments particularly gypsum and combinations of gypsum with organic matter. Sodium was the dominant cation present in saturation paste extracts and leaching reduced concentrations of Ca, Mg, K and Na in extracts (Table 5.3). Concentrations of Ca in extracts were significantly increased by gypsum additions. Concentrations of Al in extracts were increased by leaching where no gypsum was added. SAR in extracts was reduced by amendments (particularly gypsum) and significantly reduced by leaching (Table 5.3).

5.3.3 Microbial properties

Organic C content of samples was significantly increased by additions of biosolids and cattle manure and was unaffected by leaching (Fig. 5.1). Soluble organic C concentrations were increased more by additions of biosolids than cattle manure and were decreased by leaching. The C/N ratio of organic matter was increased by additions of cattle manure. As expected, microbial biomass C was increased by additions of the organic amendments and this effect was more pronounced for biosolids (Fig. 5.1). Values were lower in leached than unleached treatments. Basal respiration and metabolic quotient showed broadly similar trends being most significant for the cattle manure and biosolids alone treatments and being increased by leaching.

5.3.4 Physical properties

Leaching had no significant effects on total porosity, pore size distribution, available water or water content at field capacity so mean values for unleached and leached treatments are shown in Table 5.4. Total porosity tended to be increased by additions of cattle manure and biosolids alone but pore size

distribution, available water (Table 5.4) and water content at field capacity (range 238-264 kg m^{-3}; data not shown) were unaffected by treatments.

Changes in volume of residue mud upon drying the wet paste and then rewetting are shown in Fig. 5.2a. Approximately 50% of the initial volume of mud was lost upon drying and when this dried material was then submerged in water for 5 days it had a volume only 70% of the initial volume. When the dried 5-10 and 2-5 mm fractions were wet sieved, 80% or more of aggregates were highly stable and remained on the 5 or 2 mm sieves respectively (Fig. 5.2b). When the rewetted < 2 mm fraction (either alone or mixed with amendments) in the form of a paste was dried and sieved particles larger than 2 mm were formed (Fig. 5.2c). However, when these particles (> 2 mm) were wet sieved they all broke down to particles < 2 mm diameter. That is, there was no measurable quantity of material left on the 2 mm sieve after wet sieving.

5.3.5 Plant growth and leaf nutrient content

Dry matter yields of both roots and shoots were increased by leaching in all treatments other than the control (Fig. 5.3). For control, leaching caused a decrease in yield. Biosolids additions significantly increased yields under both unleached and leached conditions. Greatest yields were recorded under leached conditions for the biosolids and biosolids plus gypsum treatments and the cattle manure plus gypsum treatment also showed relatively high yields.

Mean leaf macro-nutrient contents of Rhodes grass are shown in Table 5.5. Whilst for control leaching caused an increase in Na content, a decrease in K content and a reduction in the tissue K/Na ratio the reverse was generally the case for all the other treatments. There were no consistent trends with treatment for tissue Ca and Mg concentrations while P concentrations were increased in treatments receiving biosolids. Total N content of plants from control treatments tended to be higher than those from the others. Concentrations of tissue Cu, Zn, Mn, Fe were not consistently affected by treatments (data not shown).

Cumulative shoot mass, root mass and total plant mass were all significantly negatively correlated with EC, Na concentration and SAR in saturation paste extracts and with EC measured in water and ESP but not with pH measured in either saturation paste extracts or in water (Table 5.6).

5.4 Discussion

Physical properties of bauxite residue are considered an important impediment to plant establishment and growth (Wehr et al., 2006; Jones and Haynes, 2011). It has been reported that the low hydraulic conductivity of newly deposited mud hampers drainage and favours waterlogging in the structureless paste whilst drying causes consolidation of the mud and formation of a massive solid structure (Wehr et al., 2006). Both conditions can severely limit root growth in the material. Nevertheless, there are several examples where revegetation has been successful under field conditions (Courtney et al., 2009; Aluminium for Future Generations, 2016). In these situations, the residue has been left for 5-10 years to undergo wetting and drying cycles as well as leaching. Visual observations in the field suggest that following drying the mud solidifies and loses substantial volume. This causes cracks and macropores to depth in the residue deposit and such cracking remains after rewetting. The surface horizon of the dried material can then be tilled to produce a stable tilth suitable for plant establishment and growth. Our laboratory results confirmed and helped explain these observations.

For example, drying caused a 50% loss in volume and after subsequent rewetting the volume remained at 70% of what it was originally. This means that the volume of residue is significantly reduced by drying and much of this reduction remains following rewetting. This explains the cracking to depth that is observed in the field. Results showed that the binding reactions that occur during drying are effectively irreversible and the result of a one-off reaction that occurs during drying of the residue for the first time. That is, when dried, solidified, finely-ground (< 2 mm) material was rewetted to form a paste, mixed and then dried it did not bind together again to form stable aggregates of diameter > 2 mm. By contrast, after drying for the first time the solidified material is highly water stable. For example, we found that when dried, solidified material was broken up and sieved to form aggregates of 2-5 mm and 5-10 mm diameter, these aggregates were highly resistant to the disaggregating effects of wet sieving. Thus, when dried mud is tilled it forms a stable tilth. The larger aggregates formed are stable while the fine material is also stable and therefore does not bind together to reform a massive structure. This stability of structure is an extremely important factor in maintaining a suitable substrate for plant growth (i.e. suitable aeration and water holding capacity).

The nature of the binding agents in bauxite residue that causes solidification is a matter of controversy and a number of different compounds have been implicated (Jones and Haynes, 2011). It is, however, well known that residue mud contains pozzolanic agents and indeed this allows it to be used in cement production (Liu and Zhang, 2011; Ribeiro et al., 2011). It is thought that at least some of the pozzolanic reactions occur between the alumina phase (boemite and gibbsite), lime and gypsum which result in formation of the binding material ettringite (Basin Building Partnerships, 2016).

While experiments performed in the previous studies (Chapters 3 and 4) used sieved < 2 mm aggregates (as is the convention for soil analysis), for this research the 2-5 mm fraction was used. This was done to provide a more conducive environment for root growth (i.e. greater macroporosity) since plant growth in various treatments was being investigated. As discussed above, aggregates formed after drying are quite stable so that the particle size distribution formed by sieving remained essentially unchanged during the period of plant growth. A comparison of the results presented in Chapter 4 with those recorded here shows that the use of increased particle size resulted in a change in pore size distribution with an increase macroporosity (e.g. macroporosity 59% in Table 5.1 compared to 4% in Chapter 4), and concomitant decreases in micro and mesoporosity, as well as reductions in available water and water content at field capacity

By contrast with previous results where additions of organic amendments to < 2 mm aggregates increased macroporosity (Chapter 3) here, where macroporosity already exceeded 55%, organic amendments had no measurable effect on pore size distribution. Total porosity did, however, tend to be increased by additions of organic amendments where gypsum was not applied. In general, it appears that because the mud solidifies upon drying, and the physical properties of the growth medium can be managed by regulating the size of the aggregates formed upon breaking up the solidified mud, addition of organic matter will have only small effects on the physical properties of the tilth. Nonetheless, its addition may well be important in relation to lowering and buffering pH and also for addition and release of nutrients. For example, in this study addition of biosolids or cattle manure decreased the pH in saturation paste extracts for both unleached and leached conditions (compared to the unamended control treatments) and increased extractable Ca, Mg, K and P levels.

Because seawater neutralization results in a substantial increase in salinity of the residue (Li et al., 2016), leaching is essential prior to revegetation. However, the initial leaching of the bulk sample with one pore volume of water (i.e. in the 'unleached' treatment) was insufficient. That is, EC in saturation paste extracts ranged from 15-27 dS m^{-1} while values of > 12 dS m^{-1} are generally considered too saline for growth of most plants (Shaw, 1999). However, as noted previously (Menzies et al., 2009; Li et al., 2016), during subsequent leaching with 6 pore volumes of water there was a significant increase in pH. For example, the pH in control treatments rose from 9.1 to 10.1 when measured in water and from 8.5 to 9.6 when measured in saturation paste extracts (Tables 5.2 and 5.3). This increase demonstrates that the residue contains a residual pool of alkalinity that dissolves over time. Seawater treatment results in partial neutralization of residues through precipitation of soluble alkalinity (HCO_3^-/CO_3^{2-}) as sparingly soluble Ca and Mg hydroxides and hydroxycarbonates (particularly hydrotalcite) (Hanahan et al., 2004) and there is a consequent decrease in residue pH from 11-13 down to about 9. It is possible that upon leaching these compounds begin to redissolve

thus inducing the rise in residue pH. Crystalline hydrotalcite was not detected in the seawater neutralized residue (Li et al., 2016) and it, and similar compounds, are probably present as amorphous precursors that are not detectable by mineralogical X-ray analysis.

Other compounds speculated or known to be present in bauxite residues such as tri-calcium aluminate, cancrinite and sodalite (Dilmore et al., 2008; Khaitan et al., 2009; Menzies et al., 2009) also represent solid phase alkalinity (Grafe et al., 2011) that may be contributing to the pH increase. However, except for sodalite, these compounds were not detected by mineralogical analysis (but may well be present as poorly ordered precursors) so that it is difficult to substantiate the exact source of residual alkalinity that is contributing to the rise in pH. As noted previously (Chapters 3 and 4) the mineralogical composition of the mud includes 42% unidentified amorphous materials. A further understanding of the nature of residual alkalinity will require characterization of this amorphous phase.

In the control treatment leaching not only resulted in an increase in pH but also a pronounced decrease in Rhodes grass yields and K/Na ratio in plant tissue. Thus, from a practical viewpoint, it is clear that the leaching-induced increase in pH needs to be managed and results showed that addition of gypsum at 5% w/v more than arrested the increase resulting in a lower pH after leaching than in control treatments prior to leaching. Gypsum is a common amendment applied to residue mud prior to revegetation and it induces the precipitation of soluble alkalinity as calcium carbonate (Barrow, 1982). In addition, the added Ca displaces Na ions from cation exchange sites on the residue, and along with the added SO_4^{2-}, the Na leaches down the profile with percolating water. Thus, after leaching, treatments receiving gypsum had lower ESP and SAR values than the others. It is, however, possible that over time the precipitated residual alkalinity (i.e. calcium carbonate) induced by gypsum applications may also tend slowly dissolve causing the pH of the mud to rise. This may need to be monitored and additional gypsum added if necessary.

Amendment of the residue with cattle manure, and more particularly biosolids, also partially arrested the pH increase that occurred during leaching. This is due to these materials having a pH lower than that of the residue and possessing a significant pH buffering capacity due to the presence of humified organic material (Jones and Haynes, 2011). The addition of cations such as Ca, Mg and K in these materials also helped lower ESP and SAR compared to the control treatment.

Lack of nutrient supplying capacity and very little cycling of C, N, S and P through the organic phase are characteristics of recently deposited residues because of the lack of soil organic matter and associated microbial activity (Jones and Haynes, 2011). As expected, addition of organic wastes in the forms of cattle manure or biosolids increased organic matter content, microbial biomass C and

microbial activity (basal respiration). As noted by Grafe and Kluber (2011), accumulation and/or addition of organic matter is crucial for establishment of a heterotrophic microbial community in bauxite residues. Percolating water leached soluble C from the media amended with organic wastes resulting in lower concentrations of soluble C being present in the leached treatments. Because of this, there was less available C present as a substrate for the microbial community and as a consequence microbial biomass C was also decreased compared to unleached treatments. However, microbial activity, as estimated by basal respiration, was greater after leaching in waste-amended treatments. This is likely to be due to high salinity and sodicity limiting microbial activity in unleached treatments and the greatly reduced EC and SAR after leaching. Although metabolic quotient is used as an indicator of microbial stress (Wardle and Ghani, 1995) it can also be a reflection of factors that promote microbial activity (e.g. increased substrate availability) (Sparling, 1997). Here, the greatly reduced salinity/sodicity after leaching was a major factor promoting microbial activity (and CO_2 evolution) and thus an increased metabolic quotient.

Rhodes grass is a pervasive grass that is commonly used in drought, alkali and saline-sodic soil conditions (Russell, 1976), and has been successfully used to revegetate bauxite residue (Wehr et al., 2006; Bell et al., 1989; Meecham and Bell, 1977). Despite the tolerance of Rhodes grass to salinity/sodicity, large reductions in both parameters induced by extensive leaching greatly promoted dry matter production. This was accompanied by a general reduction in shoot Na concentration and an increase in the tissue K/Na ratio. A high Na supply can limit plant growth through a number of mechanisms and interference with the uptake and translocation of other nutrients (particularly K) is particularly important (Flowers and Lauchli, 1983). A low tissue K/Na ratio in plant shoots is known to be related to a salinity/sodicity-induced yield decreases in a number of crops (Wang et al., 2013) and effective strategies of salinity/sodicity tolerance in plants involve keeping shoot Na concentrations low and maintaining high cytosolic K/Na ratios especially in shoots (Horie et al., 2012). Leaving the residue for a sufficient period of time to allow leaching of salinity and excess Na out of the residue to occur is thus an extremely important management strategy prior to revegetation.

The pronounced increase in pH induced by leaching in the unamended control treatment (to 9.6 in saturation paste extracts) resulted in extremely poor growth and lowest dry matter yields were recorded in this treatment. Clearly, from the viewpoint of revegetation, arresting such a pH increase is of practical importance. The reason why biosolids additions increased Rhodes grass yields in unleached treatments is unclear and was probably due to a combination of factors. Nutrient supply is not likely to be a major factor because basal nutrient additions were made throughout the period of plant growth. For example, biosolids characteristically supplies large amounts of both P and N when used as an amendment (Haynes et al., 2009) but leaf tissue analysis did not reveal any obvious

deficiencies of these nutrients in any treatments. The much lower Na content of biosolids, compared with cattle manure, meant less additional Na was added to the medium and this may have contributed to the higher yields in biosolids rather than cattle manure treatments.

5.5 Conclusions

Because of pozzolanic materials present in bauxite residue mud, when it is dried for the first time its volume decreases and it solidifies to form a solid, massive structure. This dried, solidified material can be crushed/tilled to form aggregates of a desired size. Fine material formed during crushing does not re-solidify because the pozzolanic reactions are essentially irreversible and do not reoccur. Because of the stability of the aggregates formed, the material can be leached without a loss of structure. Leaching is essential in seawater neutralized residues in order to remove the excess salinity present. The increase in pH that occurs during leaching can be arrested by addition of gypsum and/or organic manures such as biosolids or cattle manure. A combination of drying the residue (then crushing and sieving it), the subsequent addition of gypsum and organic manure, followed by leaching, resulted in a growth medium that supported growth of Rhodes grass.

5.6 References

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Table 5.1 *Total elemental composition (g kg^{-1}) of the source materials.*

Material	Si	Fe	Al	Ca	K	Mg	Na	P
Residue mud	74	199	64	7.8	1.5	3.5	79.6	0.40
Biosolids	N/A*	18.6	12.9	27.5	4.3	16.7	0.96	46.5
Cow manure	N/A	19.8	10.2	12.0	7.5	6.1	2.14	6.3

*N/A = not analysed

Table 5.2 *Effects of leaching and additions of cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids to seawater neutralized residue mud on pH, EC, exchangeable (ammonium acetate-extractable) cations, extractable Al and corrected ECEC and ESP.*

Treatments		pH	EC ($dS\ m^{-1}$)	Ammonium acetate-extractable elements ($cmolc\ kg^{-1}$)					Corrected ECEC ($cmol_c\ kg^{-1}$)	ESP (%)
	Amendments			Ca	K	Mg	Na	Al		
Unleached	Control	9.1^{b}	1.5^{b}	5.6^{c}	0.33^{b}	2.5^{b}	25.9^{cd}	0.21^{c}	19.0^{a}	75^{c}
	G	8.6^{a}	4.0^{de}	5.8^{c}	0.58^{de}	3.8^{d}	24.1^{cd}	0.18^{bc}	26.3^{c}	70^{c}
	CM	9.1^{b}	3.1^{d}	16.2^{f}	0.40^{c}	3.3^{c}	24.8^{cd}	0.16^{b}	23.1^{b}	55^{ab}
	BS	9.1^{b}	1.4^{b}	7.5^{d}	0.85^{f}	3.5^{c}	27.6^{d}	0.18^{bc}	18.0^{a}	70^{c}
	G+CM	8.8^{ab}	4.9^{e}	18.2^{g}	0.67^{e}	3.5^{c}	25.1^{cd}	0.13^{ab}	26.0^{c}	53^{ab}
	G+BS	8.8^{ab}	4.6^{e}	17.0^{fg}	0.51^{d}	3.5^{c}	22.8^{c}	0.14^{ab}	24.7^{bc}	52^{ab}
Leached	Control	10.1^{d}	0.6^{a}	4.1^{a}	0.15^{a}	1.5^{a}	13.2^{b}	0.23^{c}	17.7^{a}	70^{c}
	G	8.8^{ab}	2.0^{c}	4.7^{c}	0.28^{b}	3.3^{c}	13.0^{b}	0.20^{c}	22.0^{b}	61^{b}
	CM	10.0^{d}	0.8^{a}	15.4^{f}	0.21^{ab}	2.3^{b}	11.7^{a}	0.13^{ab}	18.5^{a}	40^{a}
	BS	9.8^{c}	0.6^{a}	4.9^{b}	0.52^{d}	2.3^{b}	13.5^{b}	0.18^{bc}	18.8^{a}	64^{b}
	G+CM	8.9^{ab}	2.0^{c}	12.0^{e}	0.50^{d}	3.4^{c}	13.6^{b}	0.11^{a}	18.5^{a}	46^{a}
	G+BS	8.8^{ab}	2.0^{c}	11.9^{e}	0.30^{b}	3.5^{c}	11.5^{a}	0.11^{a}	16.5^{a}	42^{a}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$

Table 5.3 *Effects of leaching and additions of cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids to seawater neutralized residue mud on pH, EC, cations, Al and SAR in saturated paste extracts and on extractable Colwell P.*

Treatments		pH	EC	Saturated paste extract ($mmol_c\ L^{-1}$)					SAR	Colwell P
	Amendments		($dS\ m^{-1}$)	Ca	K	Mg	Na	Al	(%)	($mg\ P\ kg^{-1}$)
Unleached	Control	8.5^{b}	15.7^{c}	0.8^{a}	2.7^{c}	1.6^{a}	215.6^{d}	0.16^{ab}	207.0^{c}	9.9^{a}
	G	7.1^{a}	27.5^{e}	30.3^{d}	4.3^{c}	14.6^{c}	267.1^{e}	0.10^{a}	56.4^{ab}	8.1^{a}
	CM	7.6^{a}	19.2^{cd}	2.5^{a}	6.3^{d}	3.7^{ab}	175.6^{c}	0.13^{ab}	102.7^{b}	93.6^{c}
	BS	7.5^{a}	15.6^{c}	1.9^{a}	3.9^{c}	4.8^{ab}	178.2^{c}	0.13^{ab}	97.7^{b}	464.8^{d}
	G+CM	7.6^{a}	23.6^{d}	28.4^{d}	7.1^{d}	22.0^{d}	288.7^{e}	0.13^{ab}	57.7^{ab}	80.5^{c}
	G+BS	7.6^{a}	21.8^{d}	24.4^{c}	4.8^{cd}	22.9^{d}	253.9^{e}	0.15^{ab}	52.2^{ab}	447.4^{d}
Leached	Control	9.6^{c}	2.2^{a}	0.03^{a}	0.2^{a}	0.01^{a}	21.5^{a}	0.36^{c}	161.6^{c}	18.8^{b}
	G	7.5^{a}	8.3^{b}	17.6^{b}	1.1^{b}	7.4^{b}	90.8^{b}	0.11^{a}	25.7^{a}	11.4^{b}
	CM	8.9^{b}	3.1^{a}	0.1^{a}	1.0^{b}	0.2^{a}	28.8^{a}	0.42^{c}	72.3^{ab}	87.4^{c}
	BS	8.4^{b}	2.8^{a}	0.2^{a}	0.6^{ab}	0.4^{a}	26.2^{a}	0.20^{b}	47.9^{ab}	505.7^{d}
	G+CM	7.5^{a}	9.0^{b}	18.0^{b}	3.0^{c}	14.1^{c}	96.5^{b}	0.10^{a}	24.1^{a}	87.2^{c}
	G+BS	7.5^{a}	8.5^{b}	16.6^{b}	1.6^{bc}	16.4^{c}	98.6^{b}	0.11^{a}	24.3^{a}	426.1^{d}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$

Table 5.4 *Effects of additions of cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids to seawater neutralized residue mud on total porosity, pore size distribution and available water in bauxite residue.*

Treatment	Total porosity (m^{-3} m^{-3})	Pore size distribution (%)			Available water (kg m^{-3})
		Microporosity (< 0.2 um)	Mesoporosity (0.2-29 um)	Macroporosity (> 29 um)	
Control	0.61[a]	22[a]	19[a]	59[a]	121[a]
G	0.60[a]	22[a]	21[a]	57[a]	126[a]
CM	0.67[b]	18[a]	20[a]	62[a]	130[a]
BS	0.65[ab]	22[a]	19[a]	59[a]	119[a]
G + CM	0.61[a]	20[a]	20[a]	60[a]	123[a]
G + BS	0.59[a]	23[a]	21[a]	56[a]	128[a]

Means followed by same letters within one column are not significantly different at $P \leq 0.05$

Table 5.5 *Effects of leaching and additions of cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids on maconutrient content and K/Na ratio in leaf tissue of Rhodes grass*

Treatments		Nutrient content (g kg^{-1})						K/Na ratio
		Na	K	Ca	Mg	P	N	
Unleached	Control	64^{c}	53^{b}	9.3^{ab}	7.7^{b}	2.7^{a}	30^{b}	0.83^{c}
	CM	82^{d}	52^{b}	5.2^{a}	5.9^{a}	3.4^{b}	27^{ab}	0.64^{b}
	BS	60^{bc}	51^{b}	11.8^{c}	6.0^{a}	7.4^{d}	26^{ab}	0.85^{c}
	G	55^{b}	49^{b}	10.9^{b}	9.1^{c}	2.8^{a}	26^{ab}	0.89^{c}
	G + CM	90^{e}	48^{b}	9.5^{ab}	7.8^{b}	3.4^{b}	26^{ab}	0.54^{ab}
	G + BS	54^{b}	47^{b}	12.1^{c}	7.1^{b}	4.7^{c}	25^{ab}	0.86^{c}
Leached	Control	71^{cd}	29^{a}	5.4^{a}	5.6^{a}	2.6^{a}	31^{b}	0.41^{a}
	CM	69^{cd}	59^{c}	11.2^{c}	7.3^{b}	4.6^{c}	27^{ab}	0.84^{c}
	BS	57^{bc}	57^{c}	12.3^{c}	6.6^{b}	7.7^{d}	28^{ab}	1.0^{d}
	G	31^{a}	45^{b}	13.2^{d}	7.3^{b}	2.2^{a}	21^{a}	1.4^{d}
	G + CM	38^{a}	57^{c}	10.8^{b}	5.7^{a}	3.3^{b}	21^{a}	1.5^{d}
	G + BS	53^{b}	57^{c}	12.9^{d}	6.3^{a}	5.5^{c}	26^{ab}	1.1^{d}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$

Figure Captions

Fig. 5.1. Effects of leaching and additions of cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids to seawater neutralized residue mud on organic C, water soluble C, C/N ratio, microbial biomass C, basal respiration and metabolic quotient. Means followed by same letters are not significantly different at $P \leq 0.05$

Fig. 5.2. **(a)** Relative volume of original residue mud paste after drying and then rewetting; **(b)** size distribution of particles following wet sieving of dried 5-10 and 2-5 mm diameter aggregates and **(c)** dry sieve analysis following rewetting the < 2 mm dried aggregate fraction [mixed with nothing (Control), gypsum (G), cattle manure (CM) or biosolids (BS)] to form a paste followed by drying it again. Means followed by same letters are not significantly different at $P \leq 0.05$

Fig. 5.3. Above- and below-ground dry matter production of Rhodes grass (*Chloris gayana*) grown in unleached and leached seawater neutralized residue mud amended with cattle manure (CM), biosolids (BS), gypsum (G), gypsum plus cattle manure and gypsum plus biosolids. Means for total shoot and root mass followed by same letters are not significantly different at $P \leq 0.05$

Fig. 5.1

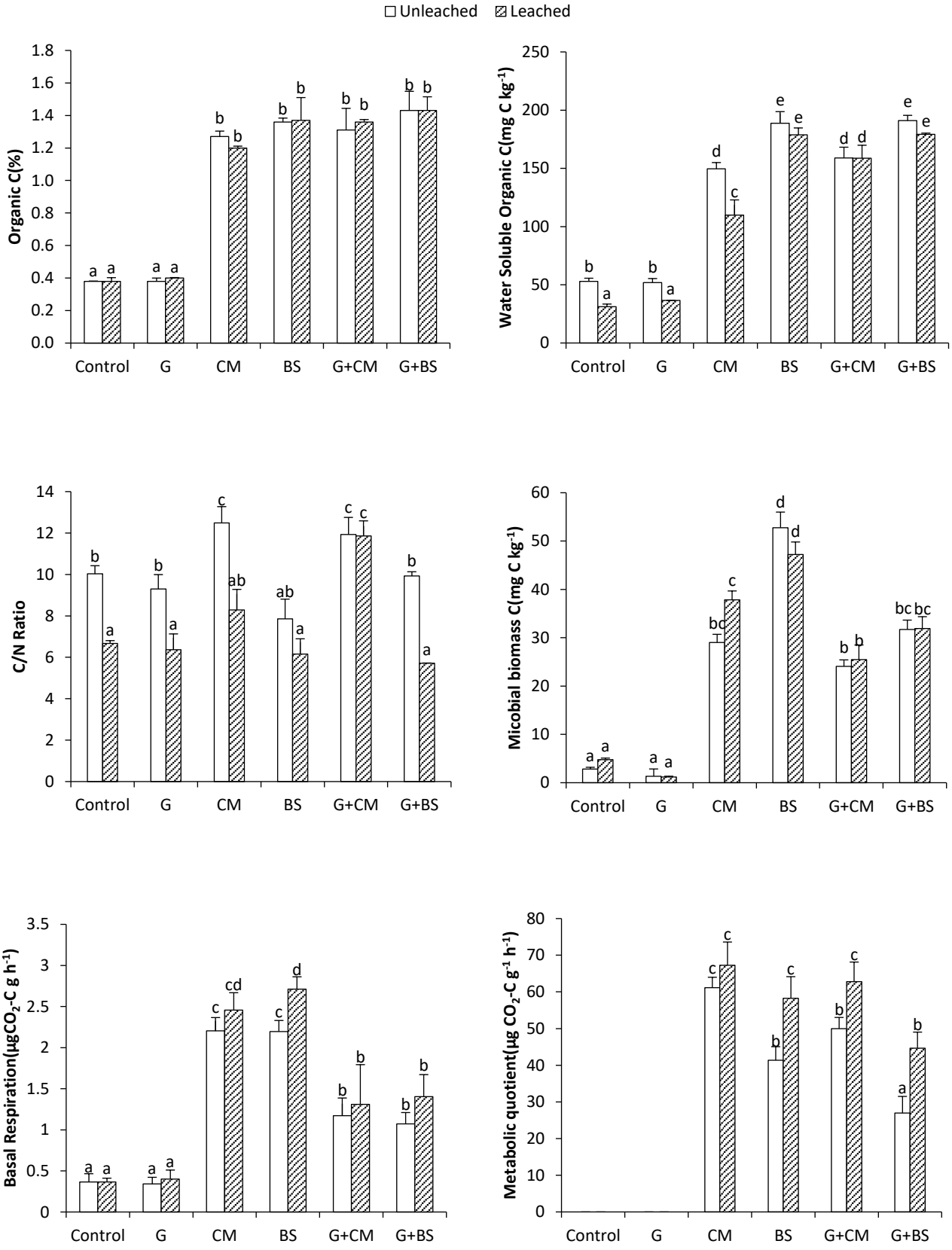

Unleached
Leached
Organic C(%)
Water Soluble Organic C(mg C kg-1)
C/N Ratio
Micobial biomass C(mg C kg-1)
Basal Respiration(µgCO2-C g h-1)
Metabolic quotient(µg CO2-C g-1 h-1)
Control
G
CM
BS
G+CM
G+BS

Fig. 5.2

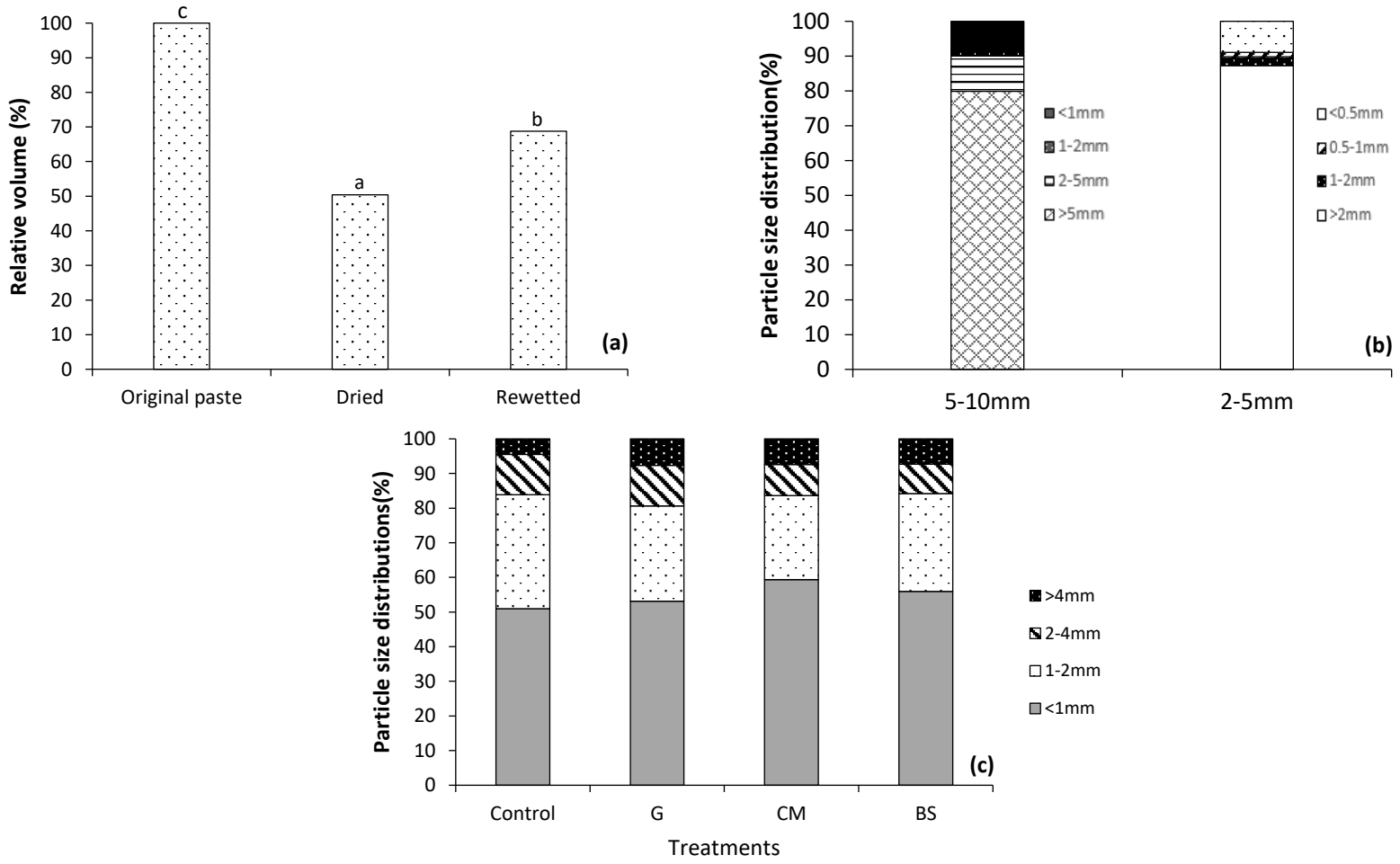
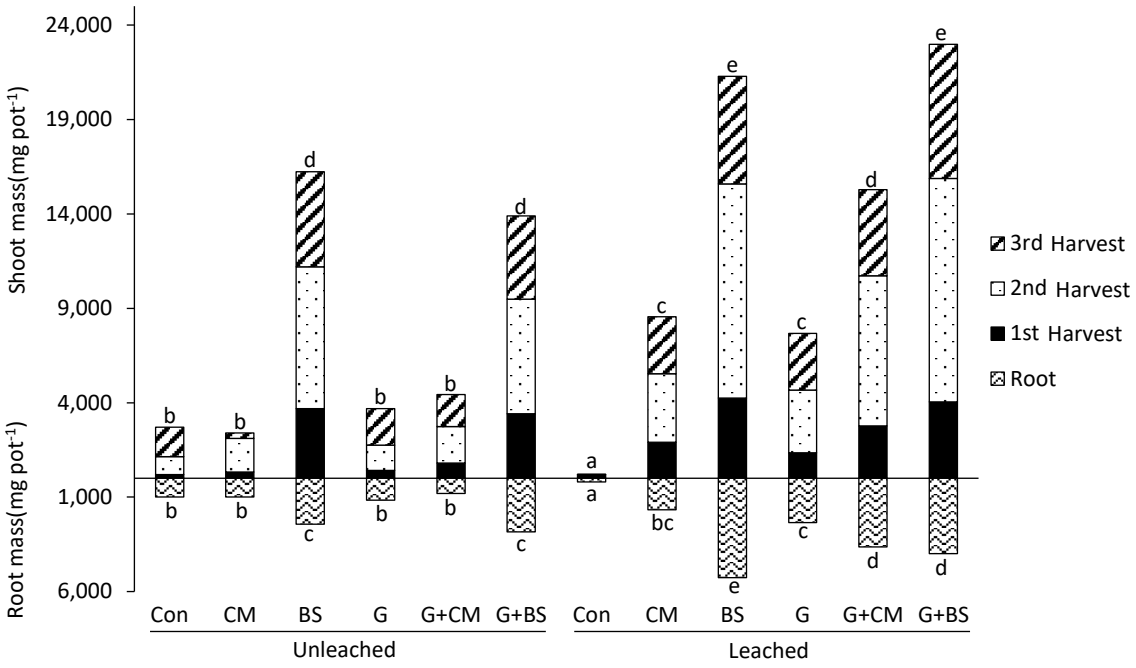

Relative volume (%)
c
a
b
(a)
Original paste
Dried
Rewetted
Particle size distribution(%)
<1mm
1-2mm
2-5mm
>5mm
<0.5mm
0.5-1mm
1-2mm
>2mm
(b)
5-10mm
2-5mm
Particle size distributions(%)
>4mm
2-4mm
1-2mm
<1mm
(c)
Control
G
CM
BS
Treatments

Fig. 5.3


Shoot mass(mg pot-1)
Root mass(mg pot-1)
24,000
19,000
14,000
9,000
4,000
1,000
6,000
3rd Harvest
2nd Harvest
1st Harvest
Root
Con
CM
BS
G
G+CM
G+BS
Unleached
Leached

6. Effect of applied amendments on the ionic composition of leachates, growth of Rhodes grass and chemical and microbial properties of seawater neutralized bauxite processing residue

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Abstract: A 32-week leaching column study was carried out in the glasshouse to investigate the effects of incorporation of gypsum, cattle manure, biosolids, gypsum plus cattle manure and gypsum plus biosolids into the topsoil (0-10 cm) on growth of Rhodes grass, and on root distribution and chemical and microbial properties in the topsoil and subsoil (10-30 cm) layers of seawater neutralized bauxite residues as well as the ionic composition of leachates. The columns were leached for a period of 8 weeks prior to sowing Rhodes grass and during that time the bulk of the salts accumulated during seawater neutralization were leached out. The main cation leached was Na^+ and the main balancing anions were Cl^- and SO_4^{2-}. During this period the pH of leachates rose from 7-8 up to 9-10 and concentrations of Al in leachates also rose. At the end of the study, exchangeable Na and pH were lowered in the surface horizon by all treatments with a combination of gypsum plus organic amendments having the greatest effect. The latter treatments also caused a significant decrease in pH in the subsoil. Organic amendments were more effective than gypsum in decreasing exchangeable Na in the subsoil layer and a combination of gypsum plus organic amendments was most effective. Rhodes grass dry matter production followed the order: Control < gypsum < cattle manure = gypsum plus cattle manure < biosolids = gypsum plus cattle manure. Growth of roots into the subsoil layer was inhibited in the Control and gypsum treatments but when organic amendments were applied, 50% or more of root dry matter was recovered in the subsoil layer. It was concluded that incorporating a combination of gypsum plus biosolids or cattle manure into the surface soil is an effective strategy for revegetation since it lowers pH and exchangeable Na in the topsoil and subsoil and promotes plant growth and root growth into the subsoil layer.

Keyword: seawater neutralisation, leaching, bauxite processing residue, gypsum, organic matter, topsoil, subsoil.

6.1 Introduction

Bauxite processing residue is the alkaline, saline, sodic waste produced during the refining of alumina (Xue et al., 2016a) and for every tonne alumina produced, 1-2 tonnes of this residue is also produced (Jones and Haynes, 2011). Since there are few uses for the residue (Klauber et al., 2011) it is typically deposited in land-based storage impoundments surrounding the refinery (Power et al., 2011). Drainage of alkaline leachate from residue storage areas is an environmental concern and must be managed for many decades after closure of the refinery. Wind-blown dust originating from the surface of the deposits is also an environmental concern. Revegetation of the storage area is a key closure strategy for most refineries since it stabilizes the surface of the deposit, reduces leaching (through loss of water via evapotranspiration) and can provide for an aesthetically pleasing environment and a wildlife sanctuary (Jones and Haynes, 2011).

In order to reduce the alkalinity of the residue, it is sometimes partially neutralized prior to its deposition in storage areas. This can be achieved by direct carbonation with CO_2 (Cooling, 2007) or treatment with seawater (Hanahan et al., 2004; Palmer et al., 2009). The alumina refineries in northern Queensland are located on the coast and the residue is seawater neutralized prior to deposition in storage areas. After neutralisation, the pH of bauxite residue is reduced from 11.0-13.0 down to about 9.0 through precipitation of soluble alkalinity as Ca, Mg hydroxides/hydroxycarbonates and hydrotalcite-like compounds (Hanahan et al., 2004; Kirwan et al., 2013). The sodicity of the residue is also decreased because Ca, Mg and K in seawater replace Na on exchange sites. As a result, seawater neutralized residue is not considered as a toxic substance (Hanahan et al., 2004) and it is presumed to be less difficult to revegetate than non-neutralized residue (A. Boullemant, personal communication, 2016)

There is, however, no research yet published on how to revegetate seawater-neutralized bauxite residue mud. Since seawater neutralization increases the salinity of residue appreciably (Hanahan et al., 2004; Chapter 3) leaching of the residue will be essential prior to attempting revegetation (Chapters 4 and 5). Previous research has shown that during leaching, the pH of the residue increases from about 9.0 up to about 10.0 due to dissolution of residual alkalinity (Chapters 3 and 4). Addition of about 5% w/v gypsum was found to be a useful amendment which arrested this pH increase (Chapter 4). Addition of organic matter (biosolids, poultry manure) was found to be an effective way

of increasing microbial activity in residue as well as adding nutrients and aiding in acidification (Chapters 4 and 5). Amendments can be readily incorporated into the surface layer (e.g. 0-10 cm) in order to improve chemical properties and promote plant root growth but, in addition, root growth into the subsoil layers can be an important consideration (Jones et al., 2012a).

In this study, the effects of incorporation of gypsum, biosolids, cattle manure, or a combination of gypsum plus biosolids or gypsum plus cattle manure incorporated into surface 10 cm of residue on leachate chemical composition, growth and nutrient uptake of Rhodes grass and chemical properties of the residue were investigated. A 32-week leaching column study was employed so that the effects of surface applications of amendments on subsoil layers could be investigated while the extent to which salts and nutrients were leached could also be quantified.

6.2 Materials and methods

6.2.1 Materials

Samples of bauxite residue were collected from an alumina refinery in north Queensland immediately after the seawater neutralisation process. The material was dried, crushed and sieved and the 5-10mm fraction was used (in order to aid drainage and promote root growth). Gypsum and cattle manure were purchased from a local garden centre. Biosolids were collected from the Oxley Creek Wastewater Treatment Plant (Brisbane). They had been treated by Cambi process (155 °C at 4.5 bar) and digested anaerobically prior to dewatering. Amendments were all air-dried, ground and sieved (< 2 mm) prior to use.

6.2.2 Experiment design

The experiment had 6 treatments including (i) control and additions of (ii) gypsum (5%v/v), (iii) cattle manure (6% w/v), (iv) biosolids (6%w/v), (v) gypsum plus cattle manure and (vi) gypsum plus biosolids. Eighteen columns (400 mm long and 150 mm inner diameter) were constructed from polypropylene pipes. These were sealed at one end with a polypropylene cap. A hole was drilled at the bottom of each column and a polyvinylchloride drainage pipe was connected. A 400 mm drainage layer of acid washed silica sand was placed in the bottom of each column. A layer of 200 mm of untreated residue was then added to each column. Treatments were thoroughly mixed with residue and added in a layer 100 mm deep above the untreated layer.

All columns were wetted to 70% water holding capacity and then incubated for 8 weeks. Columns were leached with one pore volume of water over a 24-hour period each week for the 8-week period.

This is equivalent to about 19-month rainfall at the location where the refinery is situated. Leachates were collected at each leaching event, filtered and stored in polypropylene tubes at 5 ˚C until analysed. Thirty seeds of Rhodes grass (*Chloris gayana* Kunth cv. Katambora) were then sown in each of the columns and after 10 days, seedlings were thinned to 20 per treatment. The columns were incubated for a further 24 weeks and leached with 75 mm (the mean monthly rainfall at the study locality) every two weeks. At the beginning of this period, and after each successive 6 week period, a basal dressing of N (NH_4NO_3), P ($Ca(H_2PO_4)$, K (K_2SO_4), Mg ($MgSO_4$), Mo ($NH_4Mo_7O_{24}$), Zn ($ZnSO_4$), Mn ($MnSO_4$), Cu ($CuSO_4$) and B (H_3BO_3) of 220, 25, 200, 100, 10, 10 10, 10, 10 and 4 mg kg^{-1} respectively was applied to each column. The leachate was collected and stored at 4 ˚C. At the conclusion of the experiment, above-ground herbage was harvested and then columns were cut into two (separating the surface 100 mm layer and subsurface 200 mm layer). Roots were separated and collected from the two layers, washed, dried and weighed. Above-ground herbage was rinsed twice using deionized water, oven dried at 60 ˚C, weighed and ground (< 1 mm) for subsequent elemental analysis. Topsoil and subsoil residue samples were well mixed and then split into two subsamples. One was stored at 4 °C for microbial analysis and the other was air dried and stored for chemical analysis.

6.2.3 Chemical analyses

The EC and pH of samples was measured in a 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson, 1992). Exchangeable bases (Ca, K, Na and Mg) were extracted with 1M ammonium acetate (pH 7) (1:5 w/v for 1 h) (Rayment and Higginson, 1992) and analysed by ICP-AES. Exchangeable Al was analysed in 1M KCl extracts (1:10 w/v for 1 h) by ICP-AES. Exchangeable sodium percentage (ESP) was calculated as the percentage of exchangeable bases present as Na. Saturated paste extracts were prepared and extracted under vacuum. EC and pH in extracts were measured using a glass electrode and Ca, Mg, K, Na and Al by ICP-AES. Bicarbonate-extractable P was extracted with 0.5M $NaHCO_3$ (pH 8.5) (1:100 w/v for 16 h) (Colwell, 1963) and measured colorimetrically by the molybdenum blue method. Total organic C and N content of residue were measured by dry combustion using a Carlo Erba C, H, N analyser (Rayment and Higginson, 1992).

Leachate samples were analysed for Al, Ca, K, Mg, Na, P (ICP-AES), Cl, NH_4^+, NO_3^- (Seal automated discrete analyser), SO_4^{2-} (HPIC) and pH and EC using a pH/conductivity meter. The total N content in plant samples was measured as outlined above. Plant samples were digested in nitric-perchloric acid and the content of Ca, Mg, K, Na, Al, Fe, Mn, Cu, Zn, Pb, Cd, Cr, and B in the extracts was

analysed by ICP-AES while P was determined colorimetrically. The total content of P, K, Ca, Mg Si, Al and Fe in cattle manure was determined after nitric/perchloric acid digestion and that in the biosolids and bauxite residue after microwave digestion using HF, HCl and HNO_3.

6.2.4 Microbial properties

Microbial biomass C was calculated based on the difference between organic C extracted with 0.5M K_2SO_4 from chloroform-fumigated and unfumigated samples using a K_c factor of 0.45 (Wu et al., 1990). Soluble C in the K_2SO_4 extracts was analysed using a Shimadzu 5000A soluble C/N analyser. Basal respiration was determined by placing 30 g oven-dry equivalent of most samples in a 50 mL beaker and incubating the sample in the dark for five days at 25 ˚C in a 2-L air-tight jar with 10 mL of 1M NaOH. The CO_2 evolved was determined by titration (Anderson, 1982). The metabolic quotient was calculated as basal respiration (mg CO_2-C g^{-1} h^{-1}) expressed per gram of biomass C.

6.2.5 Statistical analysis

The statistical significance of experimental treatments was determined by subjecting the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test. The relationships between shoot mass, root mass and total dry matter and various measures of salinity/sodicity and shoot tissue Na, K and Al concentrations in the treatments were fitted to linear, quadratic and cubic regression functions. Since quadratic and cubic functions did not show better fits, linear fits are reported below.

6.3 Results

6.3.1 Properties of the materials used

The composition of seawater-neutralized bauxite residue was dominated by Fe, Si, Al and Na (Table 6.1). Cattle manure and biosolids contained similar amounts of Fe and Al while the Ca, Mg and P content was greater for biosolids than cattle manure. The pH of residue mud, cattle manure and biosolids was 9.3, 6.9 and 7.2 respectively. The EC of cattle manure was relatively low while that of biosolids and residue mud was considerably higher (4.1 and16.5 dS m^{-1} respectively) (Table 6.1). The total N content of cattle manure was 2.2 g kg^{-1} and that for biosolids was 55.5 g kg^{-1}.

6.3.2 Leachate composition

The pH, EC and concentrations of the major cations and anions present in leachates over the 32-week period of the experiment are shown in Figs. 6.1, 6.2, 6.3 and 6.4 while mean values are presented in Table 6.2. The EC and concentrations of Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^- and SO_4^{2-} all declined rapidly during the pre-leaching period and most of the ions were leached during the first four weeks. At the end of the of the experiment, Na^+, Cl^- and SO_4^{2-} concentrations in leachates were below 10 $mmol_c\ L^{-1}$ while those of most of the other ions were below 1 $mmol_c\ L^{-1}$. The dominant cation in leachates was Na^+ and the main balancing anions were Cl^- and SO_4^{2-}. In the control treatment Cl^- was the dominant anion and it was also present in highest concentrations in the G, CM and BS treatments but for GCM and GBS, SO_4^{2-} was present in highest concentrations.

Addition of gypsum to treatments resulted in higher concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} being present in leachates. While addition of cattle manure had little effect on ionic concentrations in leachates, addition of biosolids increased concentrations of $H_2PO_4^-$, NO_3^-, NH_4^+ and K^+. Notably high concentrations of $H_2PO_4^-$ were present in leachates from the biosolids alone treatment during the 4-8 week period (Fig. 6.2). In all treatments, the pH of leachates increased over the pre-leaching period from 7-8 up to 9-10 and concentrations of Al also increased. Over most of the period, the control treatment had the highest leachate pH and it also had the highest Al concentrations in leachates. The $\sum C$-$\sum A$ concentration (which is mainly composed of HCO_3^-/CO_3^{2-}) was greatest in the control, CM and BS treatments which also had the highest pH values.

6.3.3 Grass yield and leaf nutrient content

Both shoot and root dry matter yields followed the trend: control << G < CM = GCM << BS = GBS (Figure 6.5). For control, the shoot mass was limited, and the roots failed to reach the subsurface layer. By adding gypsum alone, the yield was more than doubled but there was little root penetration into the subsoil layer. For the CM, BS, GCM and GBS treatments, there was appreciable root growth into the unamended subsoil (10-30 cm) layer with about 50% of the root mass being present in that layer.

In comparison with nutrient levels reported by other workers for Rhodes grass (Smith, 1974; Mesa and Mendoza, 1986) there were no obvious nutrient deficiencies in shoot tissue for any of the treatments (Table 6.3). Plants from the control treatment contained very high concentrations of Na (36.2 $g\ kg^{-1}$) as well as Al, Fe and Cu (Table 6.3). The K/Na ratio in tissues were notably low for the

Control treatment. Concentrations of tissue Mn, Zn, B, Pb, Cd and Cr showed no consistent trend with treatment (data not shown).

Regression analysis showed no significant trends between shoot, root or total plant mass and pH, EC, exchangeable cations, extractable Al or Ca, Mg, K, Na or Al content of saturation paste extracts (data not presented). However, SAR in saturation paste extracts was significantly negatively correlated with root, shoot and total plant mass and ESP was also negatively related to total plant mass (Table 6.4). Tissue Na and Al contents in Rhodes grass plant tops were also negatively correlated with root, shoot and total plant mass (Table 6.4).

6.3.4 Chemical properties

The pH of the residue after the 32-week experiment ranged from 8.8-9.9 in the topsoil and 9.7-10.0 in the subsoil (compared with an initial pH of 9.3) (Table 6.5). The final pH of the topsoil for the G and GCM treatments was 9.0 and that of the GBS treatment was 8.8. By contrast, in the control treatment the pH increased to 9.9 in the topsoil and 10.0 in the subsoil. In comparison with the Control, subsoil pH was reduced to 9.7 in the GCM and GBS treatments. As expected, due to regular leaching, EC was low in all treatments (Table 6.5).

Exchangeable K and extractable Al were unaffected by treatment but exchangeable Ca was increased by addition of all the amendments in both the topsoil and subsoil (Table 6.5). The gypsum and GCM and GBS treatments elevated exchangeable Ca the most. Exchangeable Mg was also increased by addition of amendments with cattle manure and biosolids having a greater effect than gypsum in both the topsoil and subsoil. By comparison with Control, addition of all amendments lowered exchangeable Na and ESP values in both the topsoil and subsoil. Treatments including CM and BS had a greater effect in lowering subsoil exchangeable Na/ESP than gypsum alone. The GCM and GBS treatments had the lowest values for exchangeable Na in both topsoil and subsoil (Table 6.5). There was no discernible trend in ECEC values with treatment. Colwell P was increased by additions of cattle manure and more particularly biosolids. For treatments amended with organic materials, addition of gypsum (GCM and GBS) markedly increased extractable P levels in the topsoil layer but decreased it in the subsoil.

For brevity, the content of saturation paste extracts is not shown. Their content of Ca, Mg, K, Na and Al showed similar trends with treatment to exchangeable Ca, Mg, K and Na and extractable Al. SAR showed similar trends to ESP being reduced by addition of all amendments in the subsoil and more

particularly the topsoil. A combination of gypsum plus biosolids or cattle manure had the greatest effect in reducing SAR in both the topsoil and subsoil.

6.3.5 Organic matter and microbial properties

Addition of both CM and BS increased organic C and soluble C content in the topsoil layer but had no effect on values in the subsoil (Fig. 6.6). Addition of CM and BS increased microbial biomass and basal respiration in both the topsoil and subsoil layers. There were no discernible trends with treatment for values of metabolic quotient (data not presented).

6.4 Discussion

As already noted, leaching is essential prior to revegetation of seawater neutralized residues in order to remove the high salt content that accumulates during seawater neutralization. During the pre-leaching the vast bulk of the accumulated salts were removed. The ionic composition of leachates from seawater neutralized residue differed greatly from non-neutralized residues where HCO_3^-/CO_3^{2-} (as calculated by ΣC-ΣA) were the dominant anions leaching with the Na^+ (Jones et al., 2012). In this study the main cation present in leachates was, as expected, Na^+ but it was balanced predominantly by the anion Cl^- (and SO_4^{2-} particularly where gypsum had been applied). As observed in a previous study (Li et al., 2016), during leaching period the pH of leachates increased from 7-8 up to 9-10 and this is attributable to dissolution of residual alkalinity present in the residue. Such alkalinity includes solid phase alkalinity precipitated during seawater neutralization (sparingly soluble Ca and Mg hydroxides and hydroxycarbonates) (Hanahan et al., 2004; Palmer et al., 2009) and other compounds produced during Bayer digestion (e.g. tri-calcium aluminate, cancranite and sodalite) (Menzies et al., 2009; Grafe et al., 2011). During this increase in pH there was also a concomitant increase in Al concentrations in leachates since a rise in pH results in solubilisation of precipitated $Al(OH)_3$ as soluble aluminates [e.g. $Al(OH)_4^-$].

By contrast to these results, when non-neutralized residue is leached there is a characteristic slow decrease in both residue and leachate pH as the soluble alkalinity (mainly HCO_3^- and $H_2CO_3^{2-}$) is leached out and the final pH reached is around 10 (Chapter 3, Jones et al., 2012). In the case of seawater neutralized residue, much of the soluble alkalinity has already been precipitated during seawater treatment. Nonetheless, after leaching the pH increases to about 10, the same as that for un-neutralized residue. Thus, although seawater neutralization has the short-term effect of lowering pH of the residue and its leachate, in relation to long-term management of residue storage areas, and their

revegetation, its effects are not great. That is, during leaching to remove the salts, the pH of the residue and leachate rises back up to about 10 as residual alkalinity redissolves and then leaches.

Addition of gypsum reduces the pH of residues by releasing Ca^{2+} into solution thus causing precipitation of excess OH^-, $Al(OH)_4^-$, CO_3^{2-} and HCO_3^- to form $Ca(OH)_2$, tri-calcium aluminate, hydrocalcumite and $CaCO_3$ respectively (Grafe et al., 2011). The Ca^{2+} can also displace the more weakly held monovalent Na^+ ions from cation exchange sites into solution where they are susceptible to leaching (Barrow, 1982). As a result, addition of gypsum to the topsoil layer resulted in a decrease in pH and a large reduction in exchangeable Na in that layer and also a significant reduction in exchangeable Na in the subsoil layer. Although addition of cattle manure and biosolids had a lesser effect than gypsum in lowering pH and exchangeable Na in the topsoil they had a greater effect in lowering exchangeable Na in the subsoil. Both organic materials have a pH about two units lower than bauxite residue and a significant buffering capacity so they are effective acidifying agents (Jones and Haynes, 2011). Both cattle manure and biosolids contain the exchangeable cations Ca^{2+}, Mg^{2+} and K^+ (cattle manure has a notably high K content) and Mg^{2+}, and particularly the monovalent K^+, are more mobile than Ca^{2+}. They can therefore leach down into the subsoil and displace Na^+ which is then leached from that layer. The greatest effect in both decreasing pH and reducing exchangeable Na and ESP in both topsoil and subsoil layers was from a combination of gypsum and cattle manure or biosolids. This demonstrates the advantage of adding organic matter not only to add nutrients and promote microbial activity but also lower pH and exchangeable Na/ESP.

As expected, due to their high P content, additions of cattle manure and more particularly biosolids caused substantial increases in extractable P. For biosolids alone there was also a substantial leaching loss of P. Interestingly, addition of gypsum with the organic amendments resulted in an increase in extractable P in the topsoil, a decrease in extractability in the subsoil and a reduction in leaching of P (especially in the biosolids treatments). Application of gypsum to lower P mobility and reduce leaching of P from agricultural soils is well documented (Stout et al., 1998; Favaretto et al., 2012) and is primarily attributable to enhanced precipitation of Ca phosphates. Such precipitated P is extractable in the 0.5M sodium bicarbonate (pH 8.5) extractant used here since it was developed for to enhance Ca phosphates in calcareous soils (Olsen et al., 1954).

Rhodes grass is known to be highly tolerant of saline/sodic, alkaline soil conditions. For example, Gupta and Abrol (1990) observed that it grew satisfactorily in soils with an ESP of 60-70%. For this reason, it has previously been used in the successful revegetation of bauxite residues (Bell and Meecham, 1978; Wehr et al., 2006). Despite this, conditions in the Control bauxite residue treatment were extremely harsh and greatly inhibited Rhodes grass growth. Salinity, sodicity and alkalinity are

all known to be limitations to plant growth in bauxite residues (Jones and Haynes, 2011; Grafe and Klauber, 2011). However, the extensive leaching resulted in an EC in residues of 0.6-1.0 dS m^{-1} which is unlikely to be toxic to most plants (Shaw, 1999). Nonetheless, the very high concentrations of Na, Al and Fe in Rhodes grass tissue from control treatments suggests toxicities were limiting growth. Wong and Ho (1994) had also observed similar reductions of biomass caused by Na and Fe toxicity when Rhodes grass was planted into residue mud and 2% gypsum amended bauxite residue. Furthermore, the negative correlations between dry matter yields and ESP, SAR, shoot Na and shoot Al concentrations certainly suggest that excess Na and Al supply were limiting plant growth.

Plant growth is inhibited by sodicity through a number of mechanisms. Excessive uptake and accumulation of Na leads to toxicity (Naidu and Rengasmy, 1995). Enzyme reactions can be inhibited by accumulation of Na in the cytoplasm while dehydration and death of leaf cells can occur where Na accumulates in the leaf apoplasm (Keren, 2000). In addition, high concentrations of Na in soil solution reduce Ca uptake (Kopittke and Menzies, 2005) and Ca deficiency often occurs (Kopittke and Menzies, 2005) while deficiencies of N, K, Mn, Zn and Cu have also been noted (Levy, 2000; Yadav et al., 2011). Although some previous studies have linked increased plant growth in bauxite residues to an increase in tissue K/Na ratios (Jones et al., 2012b; Chapter 5), no such trend was evident here except plants in amended treatments had a higher ratio than those from the Control treatment. To avoid sodicity being a limiting factor for plant growth, an ESP of below 15% is often recommended for soils (Sumner, 1995) but for bauxite residues such a low value is unrealistic and a value of around 40% is usually considered satisfactory (Haynes, 2015). Indeed, in this study values of 20-55% gave best plant growth.

The alkaline nature of bauxite residues is growth-limiting in a number of ways. In alkaline solutions, HCO_3^- predominates between pH 6.0 and 9.5 and CO_3^{2-} and OH^- above 9.5. Very high pH, with high concentrations of OH^-, CO_3^{2-} and HCO_3^- in solution, can impair root growth and function and nutrient translocation to leaves (Gupta and Abrol, 1990; Kopittke and Menzies, 2004). High concentrations of aluminate [$Al(OH)_4^-$] present in solution at high pH (i.e. > pH 9.0) are also phytotoxic (Fuller and Richardson, 1986; Ma et al., 2003; Stass et al., 2006; Brautigan et al., 2012). Aluminium toxicity has been forwarded as a major limitation to plant growth in unamended bauxite residues by several workers (Fuller and Richardson, 1986; Courtney et al., 2009; Woodward et al., 2008) and seemed to be a limiting factor in the Control treatment.

The effect of gypsum in lowering pH and exchangeable Na was reflected in a more than doubling in Rhodes grass dry matter yields in the gypsum compared with the Control treatment. However, root growth into the subsoil layer as still limited. By contrast, in all treatments where organic amendments

had been added, half or more of root dry matter was present in the subsoil layer. This is attributable to the effect of organic amendments in lowering exchangeable Na in the subsoil layer. Lack of extensive root growth into the untreated subsoil layers is a potential problem when revegetating bauxite residue and it is suspected to be one reason for poor overall growth during revegetation (Jones et al., 2012). During dry periods of the year a deeply penetrating root system is essential for survival unless irrigation is applied. Deep root penetration allows the plant to access water and nutrients in the subsoil layers. Thus, the substantial effect of organic residues in promoting subsoil root growth is potentially of considerable practical importance.

The reason for the greater dry matter yields from the biosolids than cattle manure treatments is unclear and plant tissue analysis did not reveal any obvious cause. Although tissue P concentrations were higher in biosolids treatments, they were not low in others and extractible levels in the residue were adequate or high in other treatments. It is possible the growth promotion is related to a close synchronization between nutrient supply via mineralization (e.g. mineralization of N) and plant needs. Future research is needed to investigate the reason why biosolids had such a marked stimulatory effect on plant growth in bauxite residue.

As expected, addition of biosolids and cattle manure increased the size and activity of the microbial biomass as well as organic C and soluble C in the topsoil layer. Surprisingly, although there was no significant effect on organic C or soluble C in the subsoil layer, organic amendment additions to the topsoil increased microbial biomass C and basal respiration values in the subsoil. This is likely to have been related to the extensive root growth into the subsoil layer in these treatments and development of an active microbial community in the rhizosphere. Carbon deposition was not great enough to be detected as an increase in organic C content while after removal of roots from the subsoil layer the microbial community would have metabolized the soluble C present. Thus, as a consequence of extensive growth of roots into the subsoil microbial activity and nutrient turnover in the subsoil layer are increased.

6.5 Conclusions

Although seawater neutralization of bauxite residue lowers the pH from 11-13 down to 9, subsequent leaching results in a rise in pH up to about 10 due to dissolution of residual alkalinity in the residue. Addition of 5% gypsum into the surface horizon can arrest this pH rise in that layer and also partially alleviate Na, Al and Fe phytotoxicity. To provide for a reduction in pH and more particularly a leaching of Na from both the topsoil and subsoil layers (with a reduction in exchangeable Na/ESP),

a combination of gypsum plus organic amendments is highly effective. This allows root growth into the subsoil layers which is essential for plant survival during dry periods of the year.

6.6 References

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Table 6.1. *pH, EC and elemental composition (g kg^{-1}) of the source materials.*

Material	pH	EC (dS m^{-1})	Si	Fe	Al	Ca	K	Mg	Na	P
Seawater neutralized bauxite residue	9.3	16.5	74	199	64	7.8	1.5	3.5	79.6	0.40
Cow Manure	6.9	0.17	N/A*	19.9	10.2	12.0	7.5	6.1	2.1	6.3
Biosolids	7.2	4.1	N/A	18.6	12.9	27.5	4.3	16.7	0.96	46.5

*N/A = not analysed

Table 6.2. Mean ionic composition of leachate over the experimental period from leaching columns to which gypsum (G), cattle manure (CM) and biosolids (BS) had been incorporated into the surface layer (0-10 cm) of seawater-neutralized residue mud.

Ion	Control	G	CM	BS	GCM	GBS
pH	9.5^{b}	9.2^{a}	9.3^{ab}	9.4^{ab}	9.1^{a}	9.1^{a}
EC	3.9^{a}	5.2^{c}	4.3^{b}	4.1^{b}	5.3^{c}	5.8^{d}
Ca^{2+}	0.43^{b}	0.72^{d}	0.46^{bc}	0.21^{a}	0.52^{c}	0.84^{e}
Mg^{2+}	0.09^{a}	0.16^{b}	0.16^{b}	0.11^{a}	0.32^{c}	0.56^{d}
K^{+}	1.8^{b}	2.7^{d}	1.8^{b}	2.7^{d}	2.4^{c}	1.3^{a}
Na^{+}	45.4^{a}	56.2^{c}	48.3^{b}	43.6^{a}	49.2^{b}	57.8^{c}
NH_4^{+}	0.08^{a}	0.11^{a}	0.11^{a}	0.49^{b}	0.11^{a}	0.60^{bc}
$\sum C$	48.5^{a}	60.0^{c}	50.8^{b}	47.1^{a}	52.6^{b}	61.1^{c}
Cl^{-}	26.1^{b}	32.6^{c}	26.8^{b}	24.6^{ab}	22.9^{a}	26.3^{b}
SO_4^{2-}	10.8^{a}	25.1^{bc}	10.9^{a}	10.7^{a}	23.6^{b}	28.6^{c}
NO_3^{-}	0.16^{a}	0.17^{a}	0.54^{d}	0.30^{b}	0.43^{c}	0.48^{c}
$H_2PO_4^{-}$	0.02^{a}	0.01^{a}	0.03^{b}	0.08^{c}	0.02^{a}	0.03^{b}
$Al(OH)_4^{-}$	0.85^{c}	0.42^{b}	0.44^{b}	0.44^{b}	0.23^{a}	0.22^{a}
$\sum A$	37.9^{a}	58.3^{c}	38.7^{a}	36.1^{a}	47.2^{b}	55.6^{bc}
$\sum C$-$\sum A$	10.6^{c}	1.7^{a}	12.1^{c}	11.0^{c}	5.4^{b}	5.5^{b}

Means within one row followed by the same letter are not significantly different ($P \leq 0.05$)

Table 6.3. *Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on concentrations of nutrients in the shoots of Rhodes grass.*

Treatments	Ca	K	Mg	Na	P	S	Al	Fe	Cu	N	*K/Na*
	g kg^{-1}						mg kg^{-1}			(%)	
Control	5.1^{a}	15.4^{a}	2.1^{a}	36.2^{c}	1.9^{ab}	4.1^{c}	613^{b}	684^{d}	56^{b}	2.3^{a}	0.43^{a}
G	8.7^{c}	26.8^{b}	4.4^{b}	18.5^{b}	2.1^{ab}	4.3^{c}	520^{b}	384^{c}	48^{b}	2.3^{a}	1.4^{b}
CM	6.5^{b}	24.9^{b}	3.5^{b}	11.0^{a}	1.7^{a}	3.3^{b}	140^{ab}	100^{b}	7.7^{a}	2.9^{a}	2.3^{c}
BS	4.6^{a}	16.0^{a}	2.4^{a}	18.2^{b}	2.6^{b}	2.9^{a}	99^{a}	54^{a}	6.3^{a}	2.8^{a}	0.9^{ab}
GCM	6.1^{b}	19.6^{ab}	2.3^{a}	11.3^{a}	1.5^{a}	3.8^{c}	101^{a}	52^{a}	4.4^{a}	2.8^{a}	1.7^{b}
GBS	5.3^{a}	14.5^{a}	2.3^{a}	15.5^{a}	2.0^{ab}	3.4^{b}	106^{a}	63^{a}	6.1^{a}	2.7^{a}	0.9^{ab}

Means within one column followed by the same letter are not significantly different ($P \leq 0.05$)

Table 6.4. *Correlation coefficients (R) between Rhodes grass plant dry mass and ESP, SAR and shoot tissue Na, K, Al concentrations and tissue K/Na ratio.*

Measurement	Shoot Mass	Root Mass	Total Mass
ESP	-0.43	-0.46	-0.55*
Sat. paste SAR	-0.51*	-0.54*	-0.66**
Shoot Na	-0.51*	0.56*	-0.78**
Shoot K	-0.44	-0.41	-0.22
Shoot K/Na	-0.07	-0.01	-0.31
Shoot Al	-0.79**	0.83**	-0.95***

Level of significance shown,* $P \leq 0.05$, ** $P \leq 0.01$, *** $P \leq 0.001$

Table 6.5. *Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on concentrations of exchangeable Ca, Mg, K, Na, ESP, extractable Al, Colwell P, pH and EC in the topsoil and subsoil (10-30 cm) layers.*

Treatments	Soil layer	pH	EC (dS m^{-1})	Exchangeable cations ($cmol_c$ kg^{-1})				Extractable Al	ESP (%)	Colwell P (mg P kg^{-1})
				Ca	K	Mg	Na			
Control	Topsoil	9.9^{d}	1.0^{a}	7.1^{c}	0.3^{a}	1.8^{ab}	16.6^{e}	0.06^{a}	64.1^{cd}	20.6^{d}
	Subsoil	10.0^{d}	0.7^{a}	4.9^{a}	0.2^{a}	1.5^{a}	18.1^{f}	0.10^{b}	73.0^{e}	15.1^{b}
G	Topsoil	9.0^{b}	0.9^{a}	11.7^{d}	0.2^{a}	1.8^{ab}	6.4^{b}	0.06^{a}	31.7^{b}	22.3^{d}
	Subsoil	9.9^{d}	0.7^{a}	6.3^{ab}	0.1^{a}	2.0^{b}	17.2^{de}	0.07^{ab}	67.1^{d}	13.6^{ab}
CM	Topsoil	9.7^{c}	0.5^{a}	7.7^{c}	0.3^{a}	3.3^{d}	12.8^{c}	0.06^{a}	53.3^{c}	80.8^{f}
	Subsoil	10.0^{d}	0.6^{a}	5.7^{ab}	0.2^{a}	2.1^{b}	15.8^{d}	0.08^{ab}	66.3^{d}	16.9^{c}
BS	Topsoil	9.6^{c}	0.6^{a}	7.6^{c}	0.1^{a}	4.4^{e}	13.1^{c}	0.05^{a}	52.0^{c}	463.6^{h}
	Subsoil	10.1^{d}	0.8^{a}	5.0^{a}	0.1^{a}	2.0^{b}	16.1^{d}	0.09^{b}	69.1^{d}	42.8^{e}
GCM	Topsoil	9.0^{b}	0.7^{a}	11.5^{d}	0.2^{a}	2.6^{c}	4.9^{a}	0.05^{a}	25.1^{a}	133.2^{g}
	Subsoil	9.7^{c}	0.7^{a}	6.9^{b}	0.2^{a}	2.1^{b}	12.4^{c}	0.07^{ab}	57.1^{c}	11.9^{a}
GBS	Topsoil	8.8^{a}	0.9^{a}	17.1^{e}	0.1^{a}	3.4^{d}	5.3^{a}	0.05^{a}	20.2^{a}	532.5^{i}
	Subsoil	9.7^{c}	0.9^{a}	6.8^{b}	0.1^{a}	2.3^{b}	15.7^{d}	0.08^{ab}	63.0^{cd}	17.5^{c}

Means within one column followed by the same letter are not significantly different ($P \leq 0.05$).

Figure captions

Figure 6.1. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on pH, EC and concentrations of Na^+ in leachates. Standard errors of means shown.

Figure 6.2. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on concentrations of Ca^{2+}, K^+ and Mg^{2+} in leachates. Standard errors of means shown.

Figure 6.3. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on concentrations of $Al(OH)_4^-$, Cl^- and $H_2PO_4^-$ in leachates. Standard errors of means shown.

Figure 6.4. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in leachates. Standard errors of means shown.

Figure 6.5. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on dry matter production of Rhodes grass shoots and mass of roots in the surface (0-10 cm) and subsurface (10-30 cm) layers. Means followed by the same letter are not significantly different ($P \leq 0.05$).

Figure 6.6. Effects of incorporation of gypsum (G), cattle manure (CM) and biosolids (BS) into the topsoil layer (0-10 cm) of seawater-neutralized residue mud on organic C, soluble C, basal respiration and microbial biomass C in the surface (0-10 cm) and subsurface (10-30 cm) layers**.** Means followed by the same letter are not significantly different ($P \leq 0.05$)

Fig. 6.1

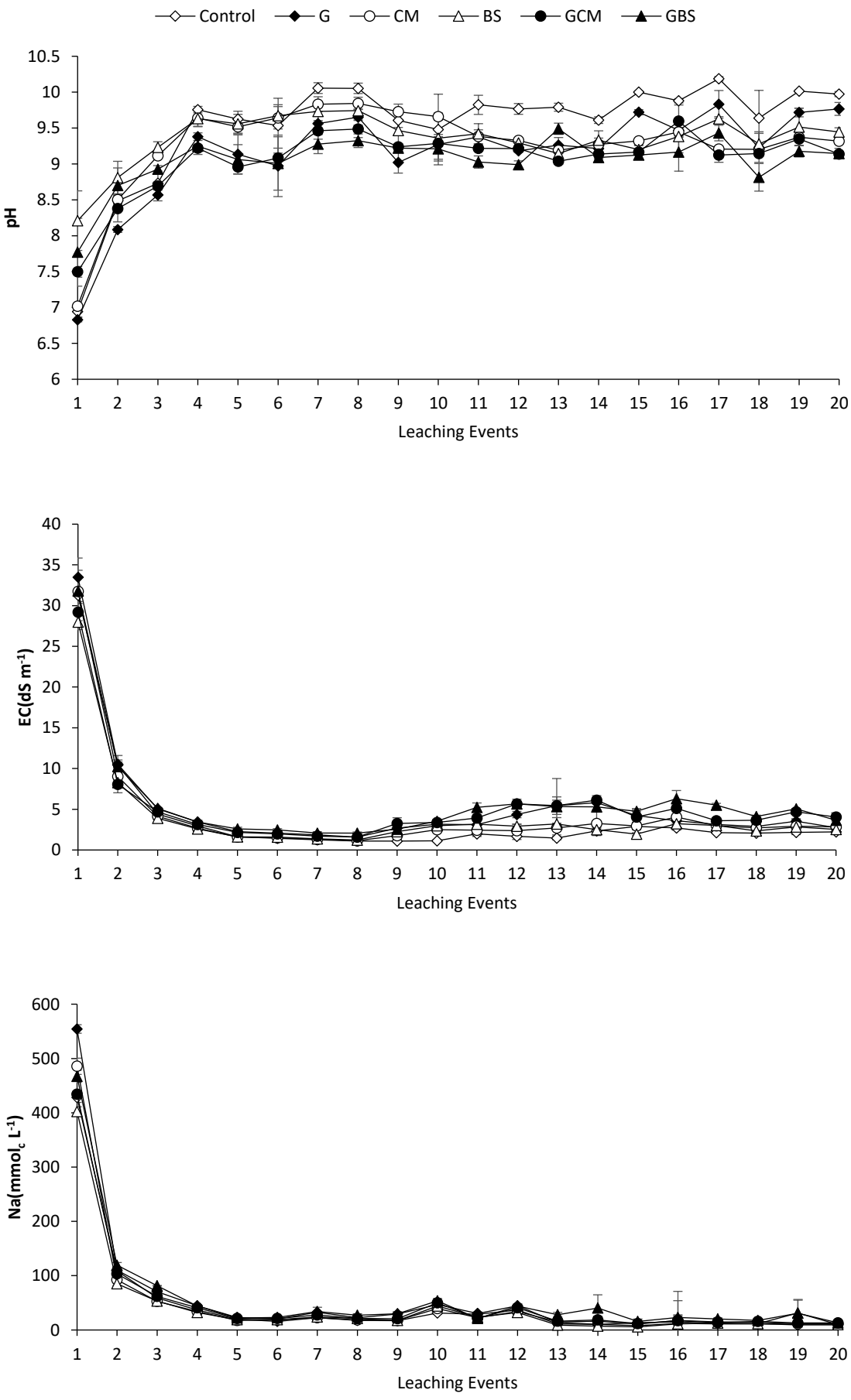

Control
G
CM
BS
GCM
GBS
pH
Leaching Events
EC(dS m-1)
Leaching Events
Na(mmolc L-1)
Leaching Events

Fig. 6.2

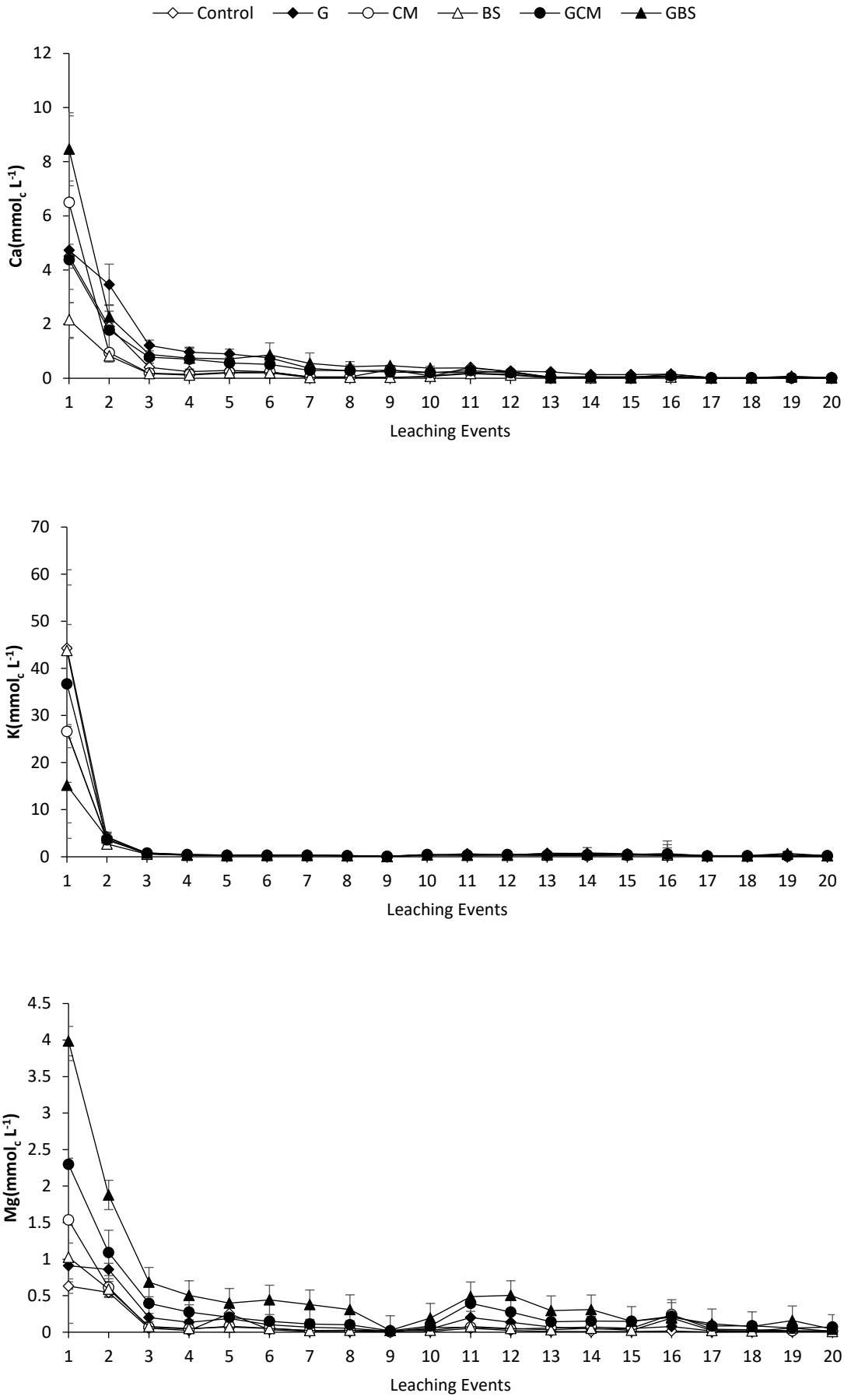

Control
G
CM
BS
GCM
GBS
Ca(mmol$_c$ L^{-1})
K(mmol$_c$ L^{-1})
Mg(mmol$_c$ L^{-1})
Leaching Events

Fig. 6.3

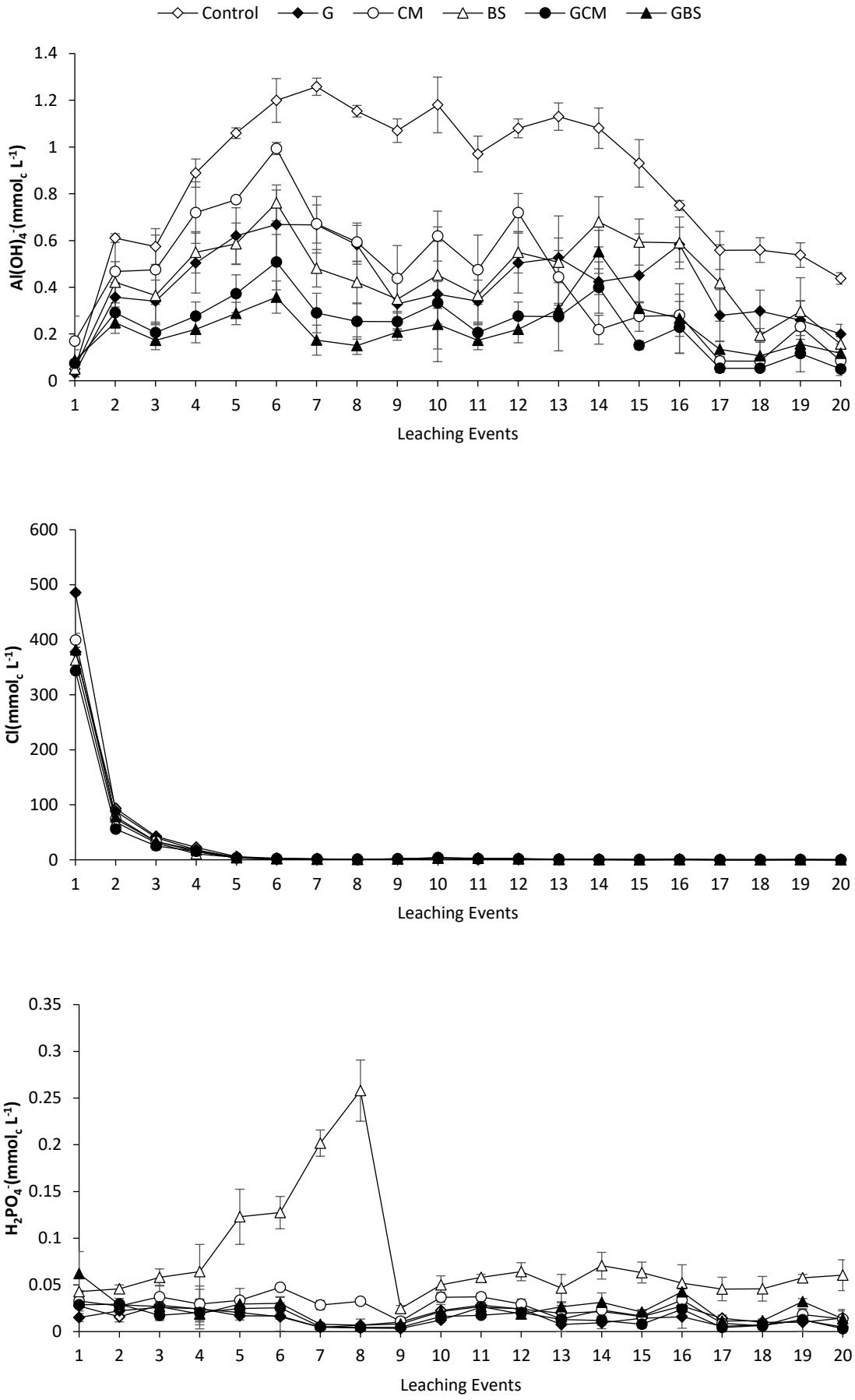

Control
G
CM
BS
GCM
GBS
Al(OH)4-(mmolc L-1)
Cl(mmolc L-1)
H2PO4-(mmolc L-1)
Leaching Events
Leaching Events
Leaching Events

Fig. 6.4

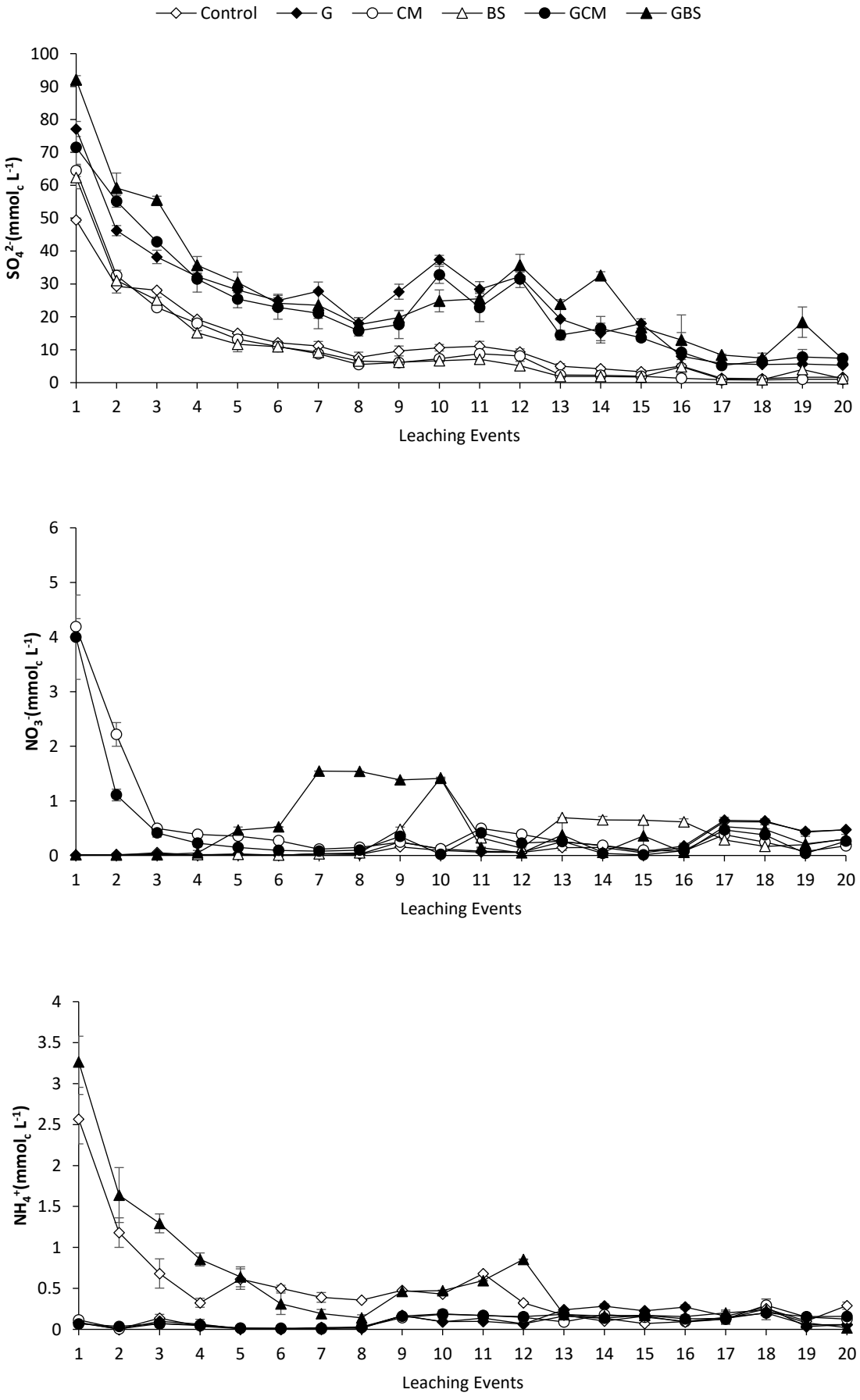

Control
G
CM
BS
GCM
GBS
SO_4^{2-}(mmol$_c$ L^{-1})
Leaching Events
NO_3^-(mmol$_c$ L^{-1})
Leaching Events
NH_4^+(mmol$_c$ L^{-1})
Leaching Events

Fig. 6.5

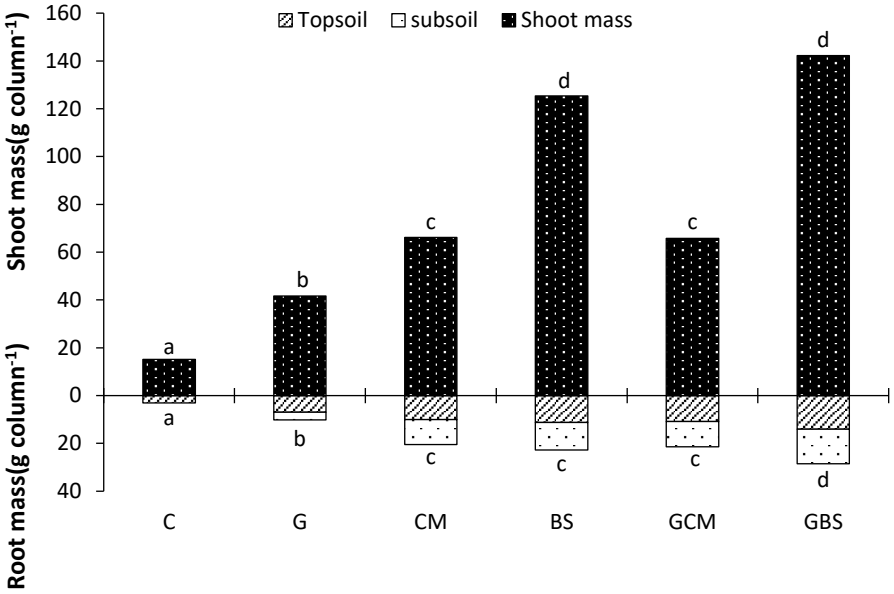
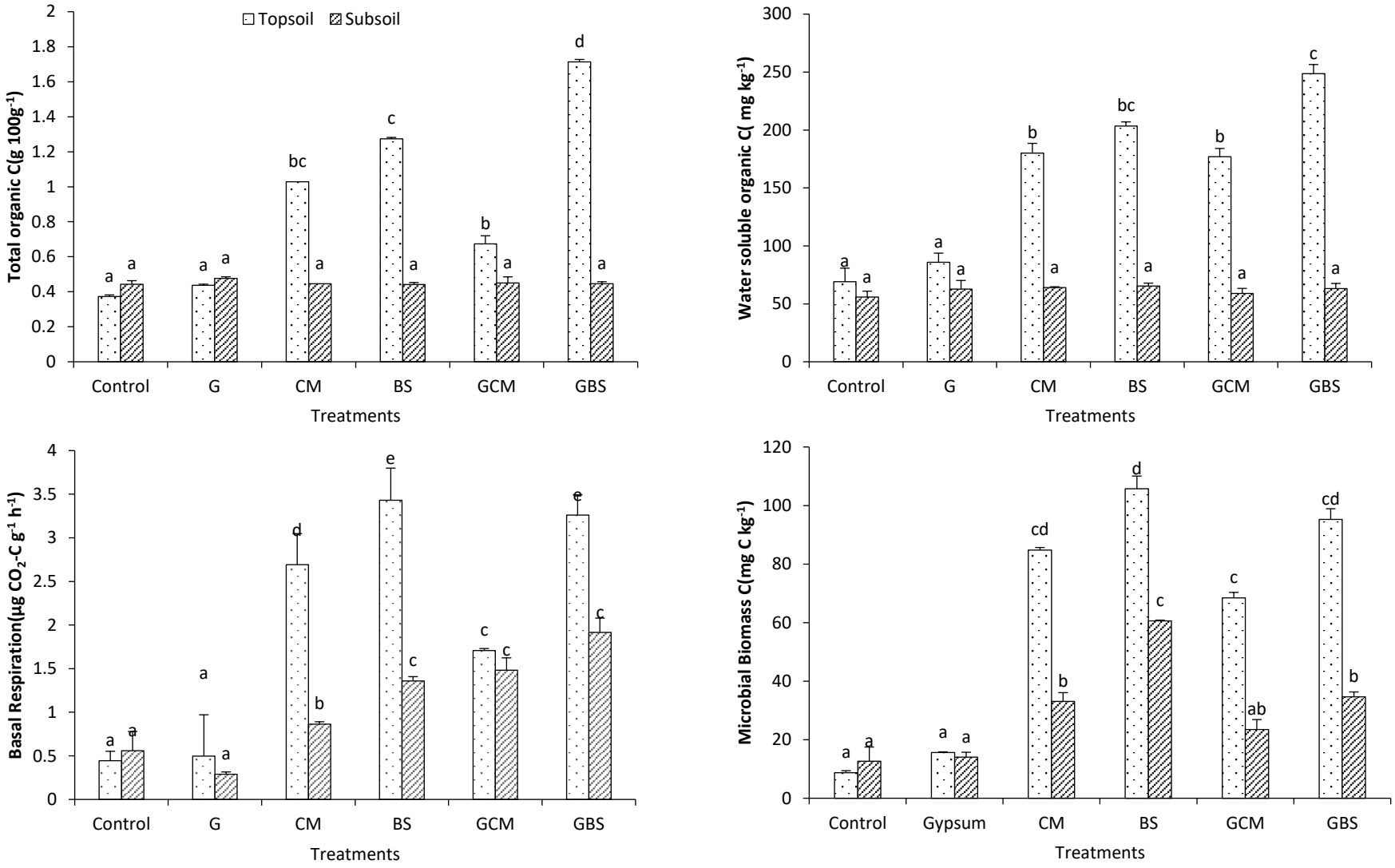

Topsoil
subsoil
Shoot mass
Shoot mass(g column-1)
Root mass(g column-1)
160
140
120
100
80
60
40
20
0
20
40
a
b
c
d
c
d
a
b
c
c
c
d
C
G
CM
BS
GCM
GBS

Fig. 6.6


Topsoil
Subsoil
Total organic C(g 100g-1)
Water soluble organic C(mg kg-1)
Basal Respiration(µg CO2-C g-1 h-1)
Microbial Biomass C(mg C kg-1)
Control
G
Gypsum
CM
BS
GCM
GBS
Treatments

7. General Discussion and Conclusions

7.1 General discussion

Previous studies in this laboratory had focussed on revegetation technologies for bauxite residue sand originating from Western Australia. Because it is bauxite with a relatively low Al content (27-30% Al_2O_3) (Anand et al., 1991) that is refined in Western Australia, about 30% of the residue produced is residue sand and this is separated from the mud. This sand material is composed of 25% Si and has a mineral component dominated by quartz (48%) (Chapter 3). It has a coarse texture, low residual alkalinity and buffering capacity. After the soluble alkalinity has leached from the material and gypsum, manures and fertilizers are added, it can be revegetated relatively easily (Cooling, 2007). Indeed, it is routine procedure to progressively revegetate the material. Such a strategy is not possible in north Queensland because sand represents only a very small percentage of the residue produced by the refineries and it is not separated from the mud prior to deposition in storage areas. This is because the far north Queensland bauxite deposit (Loughnan and Bayliss, 1961) is one of the world's highest grade deposits (49-53% Al_2O_3) and as a result very little sand (about 3% w/w) is produced. In addition, the small amount of sand particles produced have properties similar to that of the mud (Chapter 3). Thus the material to be revegetated in north Queensland is overwhelmingly residue mud.

The initial belief, prior to this study, was that because the residue mud at the north Queensland alumina refineries had been seawater neutralized, it would present considerably less challenges to revegetation than non-neutralized mud which is deposited at most other alumina refineries. Seawater neutralization reduces the pH from 11-13 down to about 9.0 and lowers the ESP of the mud (Hanahan et al., 2004). Because it has already been partially neutralized, it has been argued that *in situ* field neutralization with gypsum might well not be necessary (A. Boullemant personal communication, 2016). However, results presented in this study showed that seawater neutralization resulted in an accumulation of soluble salts (mainly originating from the seawater) in the residue to potentially phytotoxic levels where leaching is required to move salts out of the potential plant rooting volume prior to attempting revegetation. However, as has been previously reported for seawater neutralized sand (Menzies et al., 2009), during leaching the pH of the residue mud rose about one unit from 9 back up to 10 due to dissolution of residual alkalinity present in the mud. Application of gypsum at a similar rate to that typically applied to un-neutralized mud (i.e. 5%) arrested this pH increase. In addition, even after seawater treatment the ESP of the mud was high (> 65%; too high for revegetation) and the most appropriate way to alleviate this is to apply gypsum.

That is, the Ca^{2+} in gypsum ($CaSO_4 \cdot 2H_2O$) exchanges with the Na^+ on the exchange sites in the mud and the displaced Na^+ is then leached with the added sulphate anion (Jones and Haynes, 2011).

During this study it was concluded that very little is actually known about the nature of the residual alkalinity present in mud. Crystalline compounds contributing to residual alkalinity (apart from sodalite) expected to be present in the mud such as hydrotalcite and TCA (Power et al., 2011), were not detected by X-ray mineralogical analysis but it was presumed that poorly ordered amorphous precursors of such materials were present in the amorphous mineral component. Indeed, amorphous materials made up about 42% of the mineral component of the mud and are yet to be characterized. Such amorphous compounds are likely to be considerably more soluble than their thermodynamically stable crystalline counterparts and therefore be substantial contributors to the residual alkalinity present in residue mud. It seems likely that much of the residual alkalinity that dissolves during leaching is poorly ordered, sparingly soluble hydroxides and hydroxycarbonates that precipitated during seawater neutralization. Considerably more effort needs to be concentrated on identifying the nature and properties of the amorphous component of residues and its properties in both neutralized and non-neutralized residues. In particular, its contribution to residual alkalinity needs to be quantified.

Another aspect that requires future research is the nature of the pozzolanic binding compounds and their modes of action in the residues. It is a contradiction that on the one hand workers have described residue mud as being an unsuitable environment for root growth because of waterlogging in a structureless, pastey matrix of wet mud or alternatively, after drying, as being impenetrable to roots due to the formation of a massive, dense solid structure (e.g. Wehr et al., 2005). Nonetheless, there are several examples of successful revegetation (Courtney et al., 2009; Santini and Fey, 2013; Aluminium for Future Generations, 2016). Visual observations at sites where successful revegetation has been achieved suggest that upon drying the mud solidifies and loses a substantial volume. This causes cracks and macropores to form to depth in the residue deposit and such cracking remains after rewetting. The solidified surface horizon can then be ripped and tilled to form a stable tilth suitable for plant establishment and growth (Haynes, 2015). Results presented in Chapter 5 helped explain these observations. Aggregates formed after the mud was dried for the first time and then crushed/broken apart were water stable and the fine material formed upon crushing did not bind together again to form water stable aggregates. Thus, when dried mud is tilled, larger aggregates are stable while fine material is also stable and therefore does not bind together to re-form a massive structure. The results reported here on physical properties were of a preliminary nature and much more research is warranted. In particular, the nature of the pozzolanic binding materials in mud are not well characterized. However, these compounds give the mud the properties that allows a physical environment conducive to plant growth to be formed following tillage. A study of the action of these binding materials in relation to drying and subsequent tillage would be very useful.

Allowing the residue mud to dry and then breaking it up to form water stable aggregates of a desired size range produces a physical environment suitable for plant root growth. Addition of gypsum, along with organic wastes, to the mud in association with extensive leaching results in a chemical environment suitable for growth of both plants and soil microorganisms. Leaching results in removal of excess salts (partly originating from the seawater), soluble alkalinity (HCO_3^-/CO_3^{2-}) and soluble Na^+ from the rooting zone. The addition of gypsum ($CaSO_4 \cdot 2H_2O$) and organic wastes counteracts the effect of leaching in raising residue pH and the added Ca^{2+} and other cations displace Na^+ from exchange sites on the mud thus promoting leaching of additional Na^+. Drainage to a depth of several meters (e.g. drainage ditches spaced across the deposit) may be beneficial in promoting leaching. The organic wastes provide a supply of a range of macro- and micronutrients and also supply a source of soluble C that promotes soil microbial activity. Incorporation of a combination of gypsum and organic wastes into the surface horizon (0-10 cm) has the advantage of resulting in a significant decrease in pH and substantial decrease in exchangeable Na (due to its displacement and subsequent leaching) in the subsurface (10-30 cm) and this strongly promotes plant root growth into the subsoil. After application of mineral fertilizers to augment nutrient status, the mud provides an adequate medium for plant growth. Using the above strategy, revegetation of the bauxite residue storage areas in north Queensland is likely to be successful.

In the future, field studies could be initiated in northern Queensland using such a strategy to field-test its effectiveness. The first step will be draining the storage lagoons and allowing the surface few meters of mud to dry and contract/crack. This period will also allow excess salts to leach out of the surface horizons during the rainy seasons. The effectiveness of leaching can be monitored by regularly measuring EC in the surface horizon. The surface horizons can then be ripped/tilled to form a rooting zone and seedbed. Then, gypsum, organic wastes and mineral fertilizers can be incorporated into the surface horizon (i.e. 0-10 cm). Since the two refineries are close to a city, sources of organic waste in the forms of biosolids and municipal green waste are readily available. A decision on what type of saline/sodic tolerant vegetation is going to be used in revegetation needs to be made so that representative plants can be propagated and then planted into the trial site. Field trials need to be run and monitored in the relatively long-term (i.e. > 10 years) in order to ensure the sustainability of revegetation strategies and to identify and rectify any ongoing problems.

7.2 General conclusions

- Approximately 30-45% of the mineral component of bauxite residue mud is in amorphous, non-crystalline form and the nature of this component deserves detailed study.
- Bauxite residue mud contains pozzolanic agents. When dried for the first time, there is a substantial reduction in volume and the residue dries to form a solid massive structure. This material does not

disperse upon rewetting and can be crushed to form water stable aggregates of a desired size range.

- The nature and mechanisms of action of these binding agents in mud deserves future study since their actions are the basis for the formation of an adequate physical environment for plant root growth and activity.
- The seawater neutralized mud produced in north Queensland presents considerably more challenges, in relation to chemical properties that inhibit plant growth, than the residue sand produced in Western Australia.
- Seawater neutralized residue has a lower pH but a greatly increased in salinity compared with non-neutralized residue. Leaching the accumulated salts out of the potential plant root zone will be necessary prior to revegetation.
- During leaching of seawater neutralized residues the pH increases by about one unit. The nature of the residual alkalinity present in the mud that causes such a rise in pH deserves further detailed study.
- Application of gypsum, particularly in association with organic wastes (biosolids or animal manures), is required to maintain the pH of seawater neutralized residue mud at pH 9.0 or below.
- Application of the above materials (gypsum and or organic wastes) in association with leaching is required to displace excess Na from exchange sites (by the added Ca and in the case of manures Mg and K) and it can then be leached out of the root zone.
- Surface incorporation (0-10 cm) of a combination of gypsum plus organic wastes induces decreases in pH and exchangeable Na in the subsoil layers (10-30 cm) and this strongly promotes plant root growth into these subsoil layers.
- By drying and crushing residue mud to a desirable size range, adding gypsum and organic wastes and inorganic fertilizers a rooting environment suitable for growth of Rhodes grass can be provided.

7.3 Future research directions

There are a number of gaps in our basic knowledge about the composition and properties of residue mud in relation to its successful revegetation. These include the nature and properties of the amorphous mineral component (that makes up about 30-45% of the total mineral complement), the nature of the residual alkalinity present in mud (particularly in relation to the amorphous component) and the nature of pozzolanic binding agents in mud and their modes of action. These are areas that deserve detailed study. An understanding of these aspects should improve our ability to devise improved field strategies for successful revegetation.

In relation to revegetation of bauxite residue in north Queensland, a field trial should be set up and monitored to test the effectiveness of the recommendations made here. This would include (i) allowing

time for leaching of salts out the surface layers of the profile, (ii) allowing time for the mud to dry and solidify, (iii) surface tillage and incorporation of gypsum and organic wastes into the tillage layer (e.g. 0-10cm), (iv) allowing time for further leaching, (v) application of fertilizer nutrients and (vi) planting/sowing of saline/sodic-tolerant plants.

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Appendix 1

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Chemical and physical properties of bauxite residue mud and sand and the effects of leaching

Y. Li, R.J Haynes, Y-F Zhou and I. Chandrawana

Abstract - Bauxite processing residues (mud and sand) originating from a major source of bauxite being mined and processed for alumina production in Australia were collected and characterized. Mixtures consisting of 0:100, 25:75, 50:50, 75:25 and 100:0% v/v residue mud: residue sand were incubated for four weeks and a portion was then leached bi-weekly for another 14 weeks. The macroporosity of sand was much greater than that of mud whilst available water holding capacity was greater for mud. Adding increasing proportions of sand to mud decreased total porosity but increased macroporosity but the increase was only appreciable with the presence of 75% sand. The main elements present in residues were Fe, Al and Si and the main crystalline minerals present were hematite, sodalite and goethite. The amorphous component made up 32 to 42% of the mineral content. Due to seawater neutralization of the residues, they had a high EC and exchangeable Ca, Mg, K and Na content. Leaching caused a decrease in the EC of residues by at least one order of magnitude and ammonium acetate-extractable Na levels were reduced by more than half. The pH in leachates from residues increased progressively until they were about two units higher than initial values and the pH of residues also increased. This was attributed to dissolution of solid phase alkalinity present in the residue.

Index Terms - bauxite processing mud, bauxite processing residue, red mud, leaching.

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I. INTRODUCTION

Australia is the world's largest miner of bauxite and generates about 30% of the global alumina production (Geosciences, Australia, 2015). A major bauxite deposit currently being mined and refined is

in north Queensland. The deposit is one of the world's highest grade deposits (49-53% Al_2O_3) mined on a commercial scale anywhere in the world. In alumina refineries, the Bayer process is used to extract alumina by dissolving bauxite ore in hot NaOH (Power et al., 2011). For every tonne of alumina extracted, 1-2 tonnes of alkaline, saline/sodic bauxite processing residues are produced and these are deposited in residue disposal areas surrounding the refinery. At many refineries, the residues are separated into residue sand (>150 um) and residue mud (<150 um) which are deposited separately.

The north Queensland refineries do not separate the mud from the small amount of sand present but deposit residue, (after seawater neutralization) by semi-dry stacking (30% solids) between soil-based retaining walls. Seawater neutralization is a process by which the residue is reacted with seawater with the result that some soluble alkalinity (HCO_3^-/CO_3^{2-}) in the residue is precipitated as poorly soluble Ca and Mg hydroxides and hydroxycarbonates. By this process the pH of the residues is reduced from 11-13 down to about 9 (Hanahan et al., 2004).

Before revegetation of residue mud, residue sand is commonly added in order to improve aeration, drainage and root penetration (Courtney and Timpson, 2004; Courtney et al., 2009). The purpose of this study was to investigate the chemical and physical properties of seawater neutralized residues and evaluate the effect of adding residue sand to mud on soil chemical and physical properties of the substrate. The combinations used were: 100% mud, 75% mud/25% sand, 50% mud/50% sand, 25% mud/75% sand and 100% sand.

II. METHODOLOGY

A. Samples and Experiment Design

Bauxite residues were obtained from an alumina refinery in northern Queensland. The mud and sand were collected immediately following seawater neutralization and prior to their deposition in the residue disposal area. The sand made up approximately 3% of the total residue mass. Sieve analysis showed that particle size distribution of the residue sand was: >1mm, 2.3%; 0.5 – 1mm, 17.6%; 0.25 – 0.5mm, 43.8%; 0.125 – 0.5mm, 34.4%; <0.125mm, 1.9%. %.

For each residue source, five treatments were prepared consisting 0:100, 25:75, 50:50, 75:25 or 100:0% v/v residue mud: residue sand. Samples (1kg dry weight) were thoroughly mixed, rewetted to 70% water holding capacity and incubated for four weeks in a randomized block design with three replicates. A subsample was air-dried for subsequent chemical analysis while part of the moist sample was used for measurement of physical parameters and another (200 cm^3) was transferred to polypropylene leaching tubes (12 cm long and 5 cm diameter). A plug of glass wool was placed at both the top and bottom of the incubation column to prevent loss of material by downward movement of fine particles during leaching. Samples were incubated for two weeks and then leached slowly (over a 24 hour period) with one pore

volume of distilled water. One pore volume approximates to about 1.9 times the mean weekly rainfall at Gladstone (i.e. 18mm). Leachate was collected in polypropylene collecting containers and stored at 5 ºC until analysed. Following leaching, a tension of 17 kPa was applied to each column for 10 minutes to remove excess water. This process was repeated every 2 weeks for 7 leachings. At the completion of leaching, residue was removed from tubes and air-dried for subsequent chemical analysis.

B. Chemical analysis

In order to determine their mineralogy, residues were subjected to X-ray diffraction analysis. Amorphous content was calculated by difference using a corundum internal standard of known amorphous content. Exchangeable bases (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) were extracted with 1M ammonium acetate (pH 7.0) (Rayment and Higginson, 1992) analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). EC and pH were analysed in a 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson, 1992). Saturated paste extracts were prepared and extracted under vacuum. pH and EC in extracts were measured using a glass electrode and Ca, Mg, K, Na and Al by ICP-AES. For unleached samples, exchangeable Ca, Mg, K and Na concentrations were calculated by subtracting the concentrations in saturated paste extracts from those in the ammonium extracts (Jones et al., 2012). Effective cation exchange capacity was calculated as the sum of exchangeable cations (Ca, Mg, K and Na). Exchangeable sodium percentage (ESP) was calculated as the percentage of exchangeable bases present as Na. Diethylenetriminepentaacetic acid (DTPA)-extractable metals were extracted according to Lindsay and Norvell (1978) (0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M TEA: 1:2 ratio for 2h) and Zn, Cu, Mn, Fe, Pb, Cd and Cr were analysed by ICP-MS

The total content of P, K, Ca, Mg, Si and heavy metals in residue mud and sand was determined by ICP-AES after microwave digestion using HF, HCl and HNO_3. Total C and N were measured by dry combustion using a Carlo Erba C, H, N analyser (Rayment and Higginson, 1992). In order to calculate the organic C content of residues, inorganic C (HCO_3^-/CO_3-C) was removed from samples by treatment with 1 M HCl to lower pH to 4.0 over a 4 day period (with intermittent vigorous mixing). Residual acid was neutralized by raising pH to 5.0 using 0.5 M NaOH and the samples were dried at 50 ºC before analysis. Leachates were analysed for Al, Ca, K, Mg, Na, P (ICP-AES) and pH and EC using a pH/conductivity meter.

C. Physical analysis

Bulk density was determined on naturally compacted samples, particle density by the pycnometer method (Blake and Hartge, 1986) and total porosity by difference. Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Pore size distribution was calculated

as macropores (> 29 µm diameter, air-filled pores at -10 kPa), mesopores (0.2 – 29 µm diameter, drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter, water-filled pores at -1500 kPa).

D. Germination assay

A germination assay was carried out (in quadruplet) on residues before and after leaching using filter paper in petri dishes. Five mL of aqueous extract (1/10 w/v) from residues was added to dishes (Belyaeva and Haynes, 2009). Ten seeds of watercress (*Lepidium sativum*) were placed on filter paper and dishes placed in the dark at 25 ºC. The germination percentages with respect to control (distilled water) and root lengths were determined after 5 days. The germination index (GI) was calculated as $GI = \%G \times Le/Lc$, where *%G* is the percentage of germinated seeds in each extract with respect to control, *Le* is the mean total root length of the germinated seeds in each extract, and *Lc* is the mean root length of the control (Belyaeva and Haynes, 2009). The control GI value is considered as 100%.

E. Statistical analysis

The statistical significance of experimental treatments was determined by subjected the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test.

III. Results and Discussion

A. Properties of the residues

The elemental and mineralogical content of residues is a reflection of the nature of the parent ore, inputs and transformations that occur during the Bayer process plus any subsequent neutralization reactions. The main elements present in the residue mud and sand were Fe (199 and 247 g kg^{-1}), Si (74 and 101 g kg^{-1}), Al (65 and 54 g kg^{-1}) and Na (80 and 57 g kg^{-1}) respectively and equivalent values for EC were 16.3 and 7.6. The pH of both mud and sand was 9.3. Grafe et al. (2011) reported that the mineralogy of residues typically contains about 70% crystalline phases and 30% amorphous materials and in agreement with this, the mud and sand contained 42 and 32% amorphous material respectively. The main crystalline components in mud and sand were hematite (29 and 34%), sodalite (11 and 9%), boehmite (6 and 8%) and goethite 2 and 4%) respectively. The total C content of mud and sand was 7.4 and 3.8% respectively and equivalent values for organic C were 3.1 and 2.2%. Sodalite (also known as desilication product) is a sodium aluminium silicate mineral formed during the Bayer process which contributes to a slow release of Na^+ and OH^- ions from bauxite residues over time during storage (Barrow 1982; Wong and Ho, 1995). This pool of residual alkalinity present in the residue in significant quantities

means that although the residue was seawater neutralized to a pH of 9.3-9.4 (Table 1) compared to 11-13 for un-neutralized residues (Grafe et al., 2011) an increase in pH and exchangeable Na is likely to occur in the longer term, during storage

Seawater neutralization results in the replacement of some of the Na^+ on exchange sites with Ca^{2+}, Mg^{2+} and K^+ (from the seawater) and a consequent decrease in Na saturation (Hanahan et al., 2004). As a result, residues had a high initial content of Ca, Mg and K in ammonium acetate and saturation paste extracts (Tables 2 and 3). During seawater neutralization, fine mud particles (< 5 µm dia.) flocculate into larger agglomerates (80-400 µm) (Hanahan et al., 2004; Palmer et al., 2009) and the displaced cations, and those originating from the seawater, can accumulate within the agglomerates. For that reason, cations and EC in saturation paste extracts were particularly high in the mud (Table 3).

Another consequence of seawater neutralization is the precipitation of soluble alkalinity as sparingly soluble Ca and Mg hydroxides and hydroxycarbonates (e.g. hydrotalcite) and a consequent decrease in pH (Hanahan et al., 2004; Palmer et al., 2009). However, X-ray diffraction analysis did not detect crystalline compounds such as hydrotalcite suggesting they are present in non-crystalline form within the significant amorphous mineral content of residues. It is important to note that the alkalinity associated with the newly-precipitated solid phase is still present in the residue and can potentially be released over time as the materials re-dissolve (causing a pH increase).

The EC values in saturation paste extracts prior to leaching were very high ranging from 28-34 dS m^{-1} (Table 3). Indeed, an EC of > 2 dS m^{-1} is considered saline and values > 12 dS m^{-1} are generally considered too saline for most plants (Shaw, 1999). Such values underline the importance of allowing time for leaching of salts out of the profile prior to revegetation. The residues were also sodic as shown by corrected ESP values which ranged from 36-50% (Table 4) and SAR values of 72-604 (Table 3). ESP values above 10-15% and SAR values above 13 are normally considered likely to reduce plant growth (Sumner, 1993). Even after leaching, ESP values ranged from 67-82% (Table 1). Thus, although tolerance to Na can differ greatly between plant species, sodicity in all of the residue samples is likely to limit plant performance. A common practice prior to revegetation is to add gypsum ($CaSO_4.2H_2O$) to the residue. As well as resulting in some precipitation of alkalinity as calcite, the added Ca^{2+} displaces exchangeable Na^+ which leaches down the profile with the added SO_4^{2-} (Jones and Haynes, 2011). As a result, EC, SAR and ESP are greatly reduced and such a practice would be highly desirable when revegetating these materials.

Critical levels of DTPA-extractable Fe, Mn, Zn and Cu are about 4.5, 1.0, 0.8 and 0.2 mg kg^{-1} (Lindsay and Norvell, 1978) so that concentrations of Fe, Mn and Zn were low in residues (Table 4). For revegetation, fertilizer additions of macronutrients (e.g. N, P, K, and Mg) as well as Fe, Mn and Cu will be necessary.

Calculated ECEC values prior to leaching were reduced greatly when cation concentrations in saturation paste extracts were subtracted (c.f. Tables 1 and 4) and this effect was particularly evident for the mud (which had a high EC and very high concentrations of Na in saturation paste extracts). Corrected ESP values were also lowered because soil solution Na represented a proportionately greater percentage of the total ammonium acetate-extractable pool than that for other cations such as Ca and Mg (since monovalent cations are held less strongly than divalent ones) (Brady and Weil, 2007). After leaching, soluble salts were low and correction of ECEC/ESP was not necessary.

B. Effects of leaching

It is likely that the marked increase in pH of leachates (Fig. 1) and in residues (Table 1) during leaching of Weipa residues is due to dissolution of solid phase alkalinity. There are several possible sources of such alkalinity in residues including previously precipitated amorphous hydrotalcite as well as sodalite. Another possible source is tricalcium aluminate hexahydrate (TCA) which is formed when lime is added to Bayer liquor and this also accumulates in the mud (Grafe et al., 2011). This compound was not found by X-ray diffraction but it is presumed to be present within the amorphous mineral component. A proposed advantage of seawater neutralization is that the pH of mud is decreased appreciably and this will result in leachates with a lower pH. Such leachates should have much less potential for environmental damage. Work is therefore needed to determine why the pH of leachates and residues increased during leaching.

As shown in Table 5, leachate cation content was dominated by Na^+ and there were only low concentrations of Ca^{2+}, Mg^{2+} and K^+ present. The rapid decrease in EC (Fig 2) in leachates with time was mirrored in a similar decrease in Na concentrations (data not shown). This demonstrates that the excess salts in residue mud and sand are readily and rapidly leached out. As already noted, allowing adequate time for leaching is therefore and important management strategy.

C. Physical properties

Residue sand had a much greater macroporosity than mud but addition of sand to mud only had a substantial effect on increasing macroporosity when the mixture contained 75% sand (Table 6). Indeed, additions of small amounts of sand (e.g. 25%) tended to reduce total porosity and had no significant effect on pore size distribution (Table 6). Additions of sand to mud at 25% are common practice (Courtney et al., 2009) but results presented here suggest they have little effect on measured physical properties of the medium.

D. Germination index

Germination was inhibited compared to control (i.e. 100%) in all treatments to a similar extent before leaching (germination index 69-71%) but after leaching there was an increase in germination index for 75% and 100% sand (Table 1). That is, after leaching, there was still significant inhibition of germination in mud (and mixtures containing a substantial amount of mud) and these had greater ESP values than sand. As already noted, a reduction in ESP can be achieved by adding gypsum followed by leaching. Indeed, although germination percentage was satisfactory (> 65%) in all residues, most plants are unlikely to grow satisfactorily in these materials. Patterns for seed germination versus subsequent growth of plants in bauxite residues are often dissimilar (Jones et al., 2012) since longer-term physiological effects of salinity/sodicity on plant growth are not assayed in short-term germination tests.

E. Practical implications

Effectively, it is the mud component which will be revegetated at the north Queensland refineries. Although seawater neutralization has lowered pH to about 9.0, the salinity is very high and it still has a high Na content (> 68% Na saturation). Displacement of Na (e.g. with a source of Ca such as gypsum and/or organic waste) and subsequent leaching of salts will be necessary. The increase in pH (of both the mud and of leachates) that occurs during leaching of unamended residue needs further investigation. More emphasis needs to be directed towards characterizing the amorphous mineral component of residues particularly with respect to compounds that constitute residual alkalinity.

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Table 1 Effect of addition of increasing proportions of residue sand to residue mud pH, EC, ESP, ECEC and germination index before (initial) and after (final) leaching.

Sand addition (% v/v)	pH		EC (dS m^{-1})		ESP (%)		ECEC ($cmol_c$ kg^{-1})		Germination index (%)	
	Initial	Final	initial	Final	Initial	Final	Initial	Final	Initial	Final
0	9.4^{a}	9.9^{a*}	161^{e}	1.4^{d*}	73^{a}	70^{d*}	98.6^{e}	41.0^{a*}	69^{a}	75^{a}
25	9.3^{a}	10.0^{a*}	13^{d}	1.0^{c*}	74^{a}	72^{c*}	87.6^{d}	40.2^{a*}	74^{a}	68^{a}
50	9.3^{a}	10.2^{a*}	10^{c}	0.81^{b*}	73^{a}	75^{bc}	77.5^{c}	38.6^{a*}	78^{a}	72^{a}
75	9.4^{a}	10.3^{a*}	8.9^{b}	0.72^{ab*}	74^{a}	78^{b}	68.5^{b}	38.3^{a*}	71^{a}	91^{b*}
100	9.4^{a}	10.5^{a*}	7.6^{a}	0.61^{a*}	75^{a}	81^{b}	59.7^{a}	38.0^{a*}	71^{a}	93^{b*}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.
* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 2 Effect of addition of increasing proportions of residue sand to residue mud on ammonium acetate-exchangeable cations before (initial) and after (final) leaching.

Sand addition	Ca		Mg		K		Na	
(% v/v)	Initial	Final	Initial	Final	Initial	Final	Initial	Final
	19[d]	6.3[b*]	6.6[a]	5.4[d*]	1.0[b]	0.33[a*]	72[c]	29[a*]
25	16f[cd]	5.9[b*]	6.5[a]	5.0[d*]	0.99[b]	0.34[a*]	65[b]	29[a*]
50	13[c]	5.7[ab*]	6.6[a]	3.6[c*]	0.88[ab]	0.33[a*]	57[ab]	29[a*]
75	9.2[b]	5.5[ab*]	7.5[b]	2.4[b*]	0.81[a]	0.34[a*]	51[a]	30[a*]
100	6.2[a]	4.9[a*]	7.7[b]	1.8[a*]	0.78[a]	0.32[a*]	45[a]	31[a*]

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 3 Effect of addition of increasing proportions of residue sand to residue mud on pH, EC, SAR and cations in saturated paste extracts.

Sand addition (% v/v)	pH	EC (dS m^{-1})	cations ($mmol_c$ L^{-1})				SAR
			Ca	Mg	K	Na	
0	7.0[a]	34.1[c]	50.3[d]	1.6a	7.7[b]	698[c]	137[b]
25	6.8[a]	32.3[bc]	46.5[d]	4.4ab	7.5[b]	698[c]	138[b]
50	6.8[a]	31.6[b]	36.6[c]	12.5b	7.0[ab]	630[b]	127[b]
75	6.9[a]	30.8d[ab]	25.7[b]	25.2c	6.5[a]	588[ab]	119[ab]
100	6.9[a]	28.6[a]	9.0[a]	44.1d	5.9[a]	526[a]	102[a]

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

Table 4 Effect of addition of increasing proportions of residue sand to residue mud on DTPA-extractable metals and corrected (ammonium acetate minus saturation paste) exchangeable Na, ECEC and ESP.

Sand addition (% v/v)	DTPA – extractable metal (mg kg^{-1})				Exchangeable Na ($cmol_c$ kg^{-1})	ECEC ($cmol_c$ kg^{-1})	ESP (%)
	Fe	Mn	Zn	Cu			
0	0.41^{a}	0.66^{a}	0.25^{a}	1.82^{e}	11.5^{b}	30.8^{b}	36.7^{a}
25	0.49^{a}	0.68^{ab}	0.20^{a}	1.38^{d}	11.5^{b}	29.9^{b}	37.3^{a}
50	0.60^{a}	0.73^{b}	0.23^{a}	1.05^{c}	9.2^{a}	25.2^{a}	36.5^{a}
75	1.14^{a}	0.88^{c}	0.20^{a}	0.57^{b}	9.6^{a}	22.9^{a}	41.6^{ab}
100	3.16^{b}	1.28^{d}	0.25^{a}	0.21^{a}	10.0^{ab}	20.0^{a}	50.0^{b}

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

Table 5 Effect of addition of increasing proportions of residue sand to residue mud on mean ionic composition of leachates over the 7-week leaching period.

Sand addition (% v/v)	pH	EC (dS m^{-1})	Mean concentration ($mmol_c$ L^{-1})			
			Na^+	Ca^{2+}	K^+	Mg^{2+}
0	8.1[a]	28.0[a]	176.0[d]	10.5[b]	3.7[a]	0.4[a]
25	8.1[a]	26.4[a]	154.4[d]	8.1[b]	3.5[a]	1.0[b]
50	8.4[a]	24.8[a]	141.3[c]	4.6[ab]	3.6[a]	1.3[b]
75	8.8[a]	24.1[a]	131.5[b]	3.7[ab]	3.5[a]	2.1[bc]
100	9.1[a]	22.8[a]	112.9[a]	1.8[a]	3.7[a]	4.0[c]

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Table 6 Effect of addition of increasing proportions of residue sand to residue mud on physical properties

Sand addition (% v/v)	Total Porosity (m^3 m^{-3})	Pore size distribution (%)			Available Water (kg m^{-3})
		Micropores (<0.20 μm)	Mesopores (0.20-29 μm)	Macropore (>29 μm)	
0	0.66[b]	34.9[a]	65.1[c]	0[a]	454[c]
25	0.61[ab]	36.8[a]	63.2[c]	0[a]	405[b]
50	0.59[a]	37.0[a]	63.0[c]	2.1[b]	400[b]
75	0.59[a]	34.5[a]	48.4[b]	17.1[c]	286[a]
100	0.58[a]	35.0[a]	40.8[a]	24.2[d]	238[a]

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Figure Captions

Fig. 1. Effect of increasing proportions of residue sand to residue mud (0, 25, 75 and 100%) on pH of leachates during seven progressive leaching events.

Fig. 2. Effect of increasing proportions of residue sand to residue mud (0, 25, 75 and 100%) on EC of leachates during seven progressive leaching events.

Fig 1

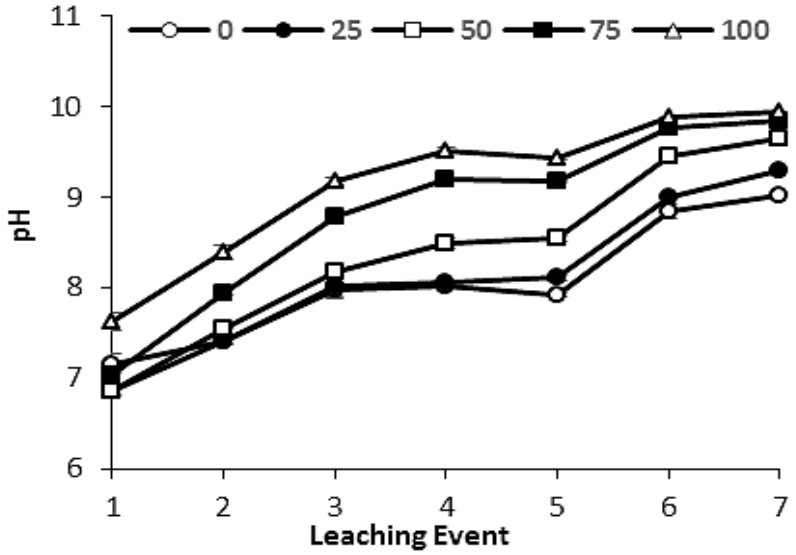
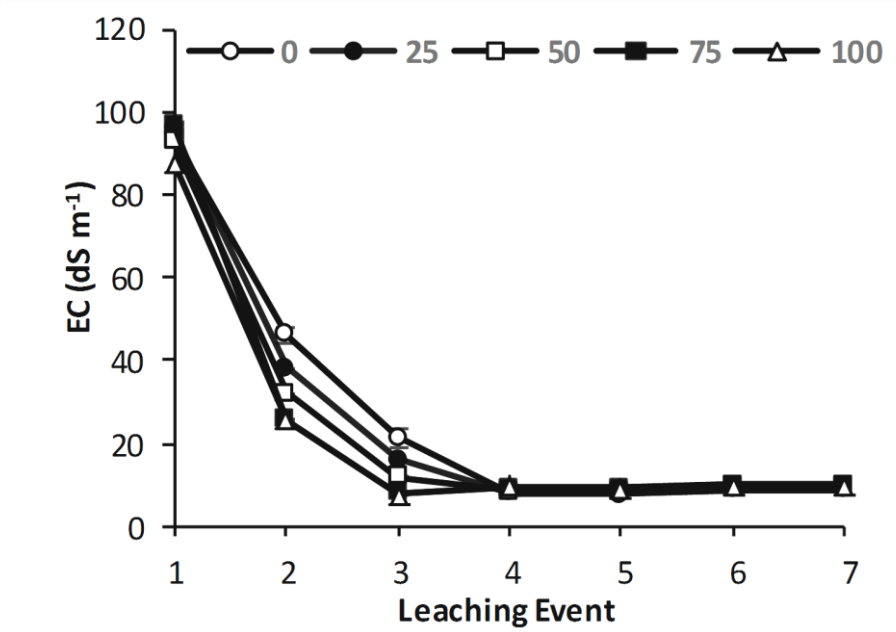

0
25
50
75
100
pH
11
10
9
8
7
6
1
2
3
4
5
6
7
Leaching Event

Fig. 2


0
25
50
75
100
EC (dS m-1)
120
100
80
60
40
20
0
1
2
3
4
5
6
7
Leaching Event

Appendix 2

(This paper has not yet been submitted for publication)

Physical and chemical properties of bauxite residue mud and sand and the effects of leaching

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Abstract Bauxite processing residues (mud and sand) originating from a Western Australian deposit were collected and characterized. The elemental content of mud and sand was Fe 191 and 158 g kg^{-1}, Al 67 and 50 g kg^{-1}, Na 37 and 3 g kg-1, and Si 104 and 247 g kg^{-1} respectively. The major mineralogical constituents for mud and sand were amorphous material 34 and 23%, goethite 22 and 10%, boehmite 3.3 and 0.4%, calcite 6.5 and 0.2%, hematite 8.5 and 11 % and quartz 7.1 and 48% respectively. Mixtures consisting of 0:100, 25:75, 50:50, 75:25 and 100:0% v/v residue mud: residue sand were incubated for four weeks and a portion was then leached bi-weekly for another 14 weeks. Residue sand had a much lower EC, exchangeable Na, ESP and short-term and residual acid neutralizing capacity than mud. Leaching caused a decrease in the EC of residues by at least one order of magnitude and ammonium acetate-extractable Na levels were reduced by more than half. The pH of the residue decreased by about one unit after leaching and leachate pH also tended to decline. This was attributed to leaching of soluble alkalinity (HCO_3^-/CO_3^{2-}) with the mobile Na^+ ion. Both short-term and residual acid neutralizing capacity were lowered following leaching. The macroporosity of sand was much greater than that of mud whilst available water holding capacity was greater for mud. Adding increasing proportions of sand to mud decreased total porosity but increased macroporosity although the increase was only appreciable with the presence of 75% sand. Further studies into the nature of the amorphous mineral component are warranted particularly in relation to the residual alkalinity present in residues.

Keywords bauxite processing mud • bauxite processing residue • red mud • red sand • leaching

Introduction

Bauxite is processed in alumina refineries by the Bayer process in which Al-containing minerals are dissolved in hot NaOH (Power et al. 2011). In 2014, 35% of bauxite production originated from Australia and on a global basis, alumina production reached 108 million tonnes (Geosciences Australia 2015). For every tonne of alumina extracted, 1-2 tonnes of bauxite processing residues are produced (i.e. approximately 120-150 million tonnes annually) and these are transferred to large land-based disposal areas surrounding the refinery. A central component of closure strategies for alumina refineries is the reclamation and revegetation of these disposal areas which may occupy hundreds of hectares of land. Successful revegetation strategies are therefore essential. Establishment and growth of vegetation is typically limited by the presence of residual NaOH in residues which confers on them a high pH (10-13) and are saline/sodic properties. Thus, leaching of the residue profile to remove excess Na^+ and accompanying soluble alkalinity (HCO_3^-/CO_3^{2-}) is essential prior to attempting revegetation (Jones and Haynes, 2011).

Bauxite residues can be separated into residue sand (>150 µm) and residue mud (<150 µm) and although large differences can exist between refineries, typically 10-20% of residue exists as sand (Jones and Haynes, 2011a). In many refineries the sand and mud are separated prior to deposition in impoundments. In order to improve the water holding capacity of residue sand before its revegetation, it has been suggested that mud can be added (Anderson et al. 2011; Jones and Haynes 2011b). On the other hand, residue sand is often added to mud before its revegetation in order to improve aeration, drainage and root penetration (Courtney and Timpson 2004; Courtney et al. 2009).

The purpose of this study was to investigate the effect of adding residue sand to mud (or mud to sand) on chemical and physical properties of the substrate and also to study the effect of leaching of residues on their chemical properties. The combinations used were: 100% mud, 75% mud/25% sand, 50% mud/50% sand, 25% mud/75% sand and 100% sand.

Materials and methods

A. Samples and experiment design

Bauxite residues were obtained from an alumina refinery in Western Australia. The sand made up approximately 30% of the total residue mass. Sieve analysis showed that particle size distribution of residue sand was : >1mm, 7.8%; 0.5 – 1mm, 24.6%; 0.25 – 0.5mm, 36.0%; 0.125 – 0.5mm, 21.5%; <0.125mm, 10.1%; and that of mud was < 2 µm 24%, 2-20 µm 54%, and 20-200 µm 22%.

For each residue source, five treatments were prepared consisting 0:100, 25:75, 50:50, 75:25 or 100:0% v/v residue mud: residue sand. Samples (1kg dry weight) were thoroughly mixed, rewetted to 70% water holding capacity and incubated for four weeks in a randomized block design with three replicates. A subsample was air-dried for subsequent chemical analysis while part of the moist sample was used for measurement of physical parameters and another (200 cm^3) was transferred to polypropylene leaching tubes (12 cm long and 5 cm diameter). A plug of glass wool was placed at both the top and bottom of the incubation column to prevent loss of material by downward movement of fine particles during leaching. Samples were incubated for two weeks and then leached slowly (over a 24 hour period) with one pore volume (calculated for residue mud) of distilled water. One pore volume approximates to about 2.3 times the mean weekly rainfall at Kwinana Beach (i.e. 15 mm). Leachate was collected in polypropylene collecting containers and stored at 5 ºC until analysed. Following leaching, a tension of 17 kPa was applied to each column for 10 minutes to remove excess water. This process was repeated every 2 weeks for 7 leachings. At the completion of leaching, residue was removed from tubes and air-dried for subsequent chemical analysis.

B. Chemical analysis

In order to determine their mineralogy, residues were subjected to X-ray diffraction analysis. Amorphous content was calculated by difference using a corundum internal standard of known amorphous content. Exchangeable bases (Ca^{2+}, K^+, Mg^{2+}, Na^+) were extracted with 1M ammonium acetate (pH 7.0) (Rayment and Higginson 1992) and analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). EC and pH were analysed in a 1:5 w/v water extract using a pH/conductivity meter (Rayment and Higginson 1992). Extractable Al was extracted with 1M KCl at (1:10 ratio for 1h) and Al analysed by ICP-MS. Saturated paste extracts were prepared (Rhoades 1982) and extracted under vacuum. pH and EC in extracts were measured using a glass electrode and Ca, Mg, K, Na and Al by ICP-AES. Effective cation exchange capacity was calculated as the sum of exchangeable cations (Ca, Mg, K and Na). Exchangeable sodium percentage (ESP) was calculated as the percentage of exchangeable bases present as Na. Bicarbonate-extractable P was extracted with 0.5M $NaHCO_3$ (pH 8.5) (1:100 w/v ratio for 16h) (Colwell 1963) and measured colorimetrically by the molybdenum blue method. Diethylenetriminepentaacetic acid (DTPA)-extractable metals were extracted according to Lindsay and Norvell (1978) (0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M TEA: 1:2 ratio for 2 h) and Zn, Cu, Mn and Fe were analysed by ICP-MS. Acid neutralizing capacity of samples before and after leaching was measured by titrating a mud/water slurry to pH 7.0, using 0.5 M HCl, over a 24 and 120-hour period. Short term (24 h) and residual (120 minus 24 h) acid

neutralizing capacity (mol H^+ kg^{-1} solid) was calculated (Snars et al. 2004). These two fractions represent soluble alkalinity and solid phase residual alkalinity.

The total content of P, K, Ca, Mg, Si and heavy metals in residue mud and sand was determined by ICP-AES after microwave digestion using HF, HCl and HNO_3. Total C and N were measured by dry combustion using a Carlo Erba C, H, N analyser (Rayment and Higginson 1992). In order to calculate the organic C content of residues, inorganic C (HCO_3^-/CO_3-C) was removed from samples by treatment with 1 M HCl to lower pH to 4.0 over a 4 day period (with intermittent vigorous mixing). Residual acid was neutralized by raising pH to 5.0 using 0.5 M NaOH and the samples were dried at 50 ºC before analysis. Leachates were analysed for Al, Ca, K, Mg, Na, P (ICP-AES) and pH and EC using a pH/conductivity meter.

C. Physical analysis

Bulk density was determined on naturally compacted samples (Haynes and Goh 1977), particle density by the pycnometer method (Blake and Hartge 1986) and total porosity by difference (Danielson and Sutherland 1986). Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Pore size distribution was calculated as macropores (> 29 µm diameter, air-filled pores at -10 kPa), mesopores (0.2 – 29 µm diameter, drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter, water-filled pores at -1500 kPa). Field capacity was determined as the volumetric water content at -10 kPa and available water as that held between -10 and -1500 kPa.

D. Germination assay

A germination assay was carried out (in quadruplet) on residues before and after leaching using filter paper in petri dishes. Five mL of aqueous extract (1/10 w/v) from residues was added to dishes (Belyaeva and Haynes 2009). Ten seeds of watercress (*Lepidium sativum*) were placed on filter paper and dishes placed in the dark at 25 ºC. The germination percentages with respect to control (distilled water) and root lengths were determined after 5 days. The germination index (GI) was calculated as $GI = \%G \times Le/Lc$, where $\%G$ is the percentage of germinated seeds in each extract with respect to control, Le is the mean total root length of the germinated seeds in each extract, and Lc is the mean root length of the control (Belyaeva and Haynes 2009). The control GI value is considered as 100%.

E. Statistical analysis

The statistical significance of experimental treatments was determined by subjecting the data to Analysis of Variance Analysis using the Minitab Software Package. Differences were calculated at the 5% level using Tukey's test.

Results

A. Properties of the residues

The sand had a lower EC and slightly higher pH than mud (Table 1). The elemental content of mud and sand was dominated by Fe, Si and Al (Table 1) and sand had a much higher Si content and lower Fe, Al, Ca, K, Mg, Na and P content than mud. The major mineralogical constituents in residues were amorphous material, goethite, hematite and quartz (Table 1). Sand had a markedly higher content of quartz and a lower content of goethite, calcite, anatase, boehmite, illite and amorphous material than mud.

Initial values (before leaching) for Colwell P, EC, ESP and ECEC were all greater in mud than sand (Table 2). Initial values for exchangeable Na and Mg were greater in mud then sand while the reverse was the case for Ca (Table 3). Before leaching the EC and concentrations of Na, K and Ca in saturation paste extracts were greater in mud than sand (Table 4) and Na was present in extracts in concentrations at least two orders of magnitude greater than those for the other cations. As a result, the SAR was very high ranging from 512 to 586 (Table 4). DTPA extractable Fe, Mn, Zn and Cu were all markedly higher in mud than sand (Table 5) and extractable Fe was one to two orders of magnitude greater than that for the other micronutrients. Organic C was low in residues (1.2 to 3.7 g kg^{-1}) although values for total C were considerably higher, particularly for mud (Table 5), due to the presence of substantial amounts of inorganic C (i.e. HCO_3^-/CO_3^{2-}). Initial values for both short-term and residual acid neutralizing capacity were an order of magnitude greater for mud than sand and progressive additions of sand to mud reduced values appreciably (Table 5).

B. Effects of leaching

Leaching caused a decrease in pH of about one unit for both mud and sand and this decrease tended to be greater in sand and with increasing proportions of sand (Table 2).The EC was reduced by one order of magnitude by leaching and ESP and ECEC were also lowered (Table 2). Concentrations of exchangeable Na were more than halved by leaching (Table 3) and concentrations of exchangeable K and Mg were also decreased for mud and 75% mud (Table 3). Concentrations of extractable Al were decreased by leaching (Table 3) principally due to the decrease in pH (Table 2). Concentrations

of cations in saturation paste extracts after leaching were, as expected, very low Na < 50 $mmol_c$ L^{-1}, Ca < 0.10 $mmol_c$ L^{-1}, Mg < 0.03 $mmol_c$ L^{-1} and K < 0.10 $mmol_c$ L^{-1} (data not presented). Leaching significantly decreased both short-term and residual acid neutralizing capacity (Table 5) and after leaching, values decreased with increasing proportions of added sand.

The mean cation content of leachates was dominated by Na^+ which was present in concentrations two orders of magnitude greater than for the others (Table 6). Both the EC and mean Na^+ concentration in leachates decreased with increasing proportions of added sand and values for mud were more than double those for sand (Table 6). Concentrations of $H_2PO_4^-$ were an order of magnitude greater in leachates from mud than sand while the reverse was the case for concentrations of $Al(OH)_4^-$.

The pH of leachates remained fairly constant throughout most of the leaching period but tended to decline at the sixth and seventh leachings (Fig 1). EC and Na^+ concentrations in leachates declined rapidly during the first three leachings (Fig 1). Concentrations of Ca^{2+}, Mg^{2+} and K^+ in leachates also declined in a similar pattern (data not shown) although their concentrations were very low throughout (Table 6).

C. Physical properties

Bulk density and particle density were greater for sand than mud and the reverse was the case for total porosity (Table 7). Addition of 50% or more sand to mud reduced total porosity (Table 7). Mud had more than three times the microporosity of sand while macroporosity was notably high in sand (Table 7). Progressive addition of sand to mud (above 50% addition) increased macroporosity and this increase was particularly notable with a 75% addition. Available water, and water held at field capacity, were greatest in mud and were progressively decreased by addition of sand to mud (Table 7).

D. Germination index

Prior to leaching, germination percentage increased with increasing proportions of added sand (Table 2). Indeed, germination was greatly inhibited by the presence of mud and the germination index was 30% or less for mixtures containing 50% or more mud (Table 2). Germination percentage was greatly increased after leaching particularly for mud and mixtures containing a high proportion of mud (Table 2). Values after leaching, were greater than 80% for all mixtures although there was still a tendency for them to increase with increasing additions of sand.

Discussion

A. Properties of the residues

The sand fraction is effectively undigested rock material and therefore contained a much greater quartz and Si content than the mud. As a result of the higher content of unreactive quartz, sand particles had a much lower ECEC than mud. This low ECEC means that retention of exchangeable cations by the material will be poor unless other materials with a higher CEC (e.g. residue mud or organic wastes such as biosolids) are added to the sand prior to revegetation. Both have previously been added to sand not only to increase cation retention but also to increase water holding capacity (Anderson et al. 2011; Jones et al. 2012a). The amorphous content of 23-34% in residues is similar to that observed for other bauxite residue samples (Grafe et al. 2011) and demonstrates that a substantial portion of the mineral fraction has not yet been characterized.

Residue mud had a notably high Colwell extractable-P content (i.e. 116.9 mg kg^{-1}) which is higher than many fertile agricultural soils (Moody and Bolland 1999). This is because the bauxite from the Darling Range is high in P (it contains 195 mg P kg^{-1}) and in Alcoa's refining process P is added as dihydrogen phosphate to control calcia (Carter 2006; Phillips and Chen 2010). Thus, although the mud is high in Fe oxides (which characteristically adsorb and sequester P) the extractable P content is still very high and higher than that for residue sand. Similarly, quantities of P leached were much greater from mud than sand. For agricultural plants, critical Colwell P levels are usually in the range of 15-30 mg kg^{-1} (Moody and Bolland 1999) but for many native Australian plants < 15 mg kg^{-1} is recommended (Handreck and Black 2002). Thus, at least in the short-term, P fertilizer applications are unlikely to be required for plant growth in mud but may well be required in sand. Nevertheless, addition of 25% mud to sand (i.e. 75% sand treatment) resulted in an increase in Colwell P into the range of 15-30 mg kg^{-1}.

The EC values in saturation paste extracts prior to leaching were very high ranging from 5.2-13.2 dS m^{-1}. Such values are likely to be detrimental to plant growth since an EC of > 2 dS m^{-1} is considered saline and values > 12 dS m^{-1} are generally considered too saline for most plants (Shaw 1999). Leaching of excess salts out of the profile will be an important management practice particularly before revegetation of mud. Values for SAR (512-604) and ESP both before (77-95%) and after (22-69%) leaching were also high since SAR values above 13 and ESP values above 10-15% are normally considered likely to reduce plant growth (Sumner 1993). Thus, exchangeable Na present on cation exchange sites will need to be displaced and then leached from the surface horizons prior to revegetation. Normally this is done by adding gypsum ($CaSO_4.2H_2O$) to the residue. The added Ca^{2+} displaces exchangeable Na^+ which leaches down the profile with the added SO_4^{2-} resulting in a

reduction in EC, SAR and ESP. Because the CEC is much higher for mud than sand, the quantity of exchangeable Na^+ retained following leaching is also greater. Thus, the quantity of gypsum added will need to be greater for mud and combinations containing a high proportion of mud.

Levels of extractable Mn and Zn were low in both mud and sand and Cu was also low in the sand. That is, critical levels of DTPA-extractable Fe, Mn, Zn and Cu are about 4.5, 1.0, 0.8 and 0.2 mg kg^{-1} (Lindsay and Norvell 1978). In addition, critical levels of exchangeable K and Mg for adequate plant growth are about 0.2-0.5 and 0.14-0.30 $cmol_c\ kg^{-1}$ respectively (Aitken and Scott 1999; Gourley 1999) so that after leaching levels of K were extremely low while Mg status was low for the sand. The lack of organic matter in the residue means there is minimal N supply (total N content 0.20-0.30 g kg^{-1}) so fertilizer N will be required for adequate plant growth. Thus, a basal fertilizer application of both macro- and micronutrients will be required prior to revegetation.

B. Effects of leaching

A decrease in pH of approximately one unit after leaching was notable for both residue sand and mud. This has been observed previously in residue sand subsoil layers where no gypsum was added (Jones et al., 2012b) and is attributable to leaching of HCO_3^-/CO_3^{2-} (soluble alkalinity) as counter-ions for the mobile Na^+ ion. That is, at the high pH of residue mud (11.0-11.3) HCO_3^-/CO_3^{2-} are the main forms of soluble alkalinity present (Jones and Haynes, 2011). As a result, there was a tendency for leachate pH to decrease with increasing leaching particularly at the sixth and seventh leaching events.

Leaching caused a reduction in EC in residues by one order of magnitude and a reduction in exchangeable Na by more than one-half. That is, Na in solution (in excess of the cation exchange capacity of the residue) was effectively removed from the residue by leaching. There was also a significant reduction in ESP since Na^+ is held less strongly to cation exchange sites than divalent cations such as Ca^{2+} and Mg^{2+} (Brady and Weil 2007) and is therefore preferentially leached from the residue. The reduction in measured ECEC after leaching occurred because the ECEC measured in residues before leaching is an overestimate of the cation exchange capacity due to the large amounts of cations present in soil solution (that are extracted with ammonium acetate). Indeed, when cations in saturation paste extracts were subtracted from ammonium acetate-extractable cations in residues (prior to leaching), calculated ECEC values decreased from 11.7-37.7 $cmol_c\ kg^{-1}$ (Table 1) down to 4-20 $cmol_c\ kg^{-1}$.

The soluble and residual alkalinity present in residues can be quantified by measuring their short-term and long-term acid neutralizing capacities (Snars et al. 2004; Grafe et al., 2011). That residue mud had values for both measurements that were an order of magnitude greater than those for sand

indicating a much greater content of reactive components in mud. The large reduction in short-term acid neutralizing capacity following leaching was expected since, as already noted, HCO_3^-/CO_3^{2-} (soluble alkalinity) leaches with Na^+. The large reduction in residual acid neutralizing capacity was less expected and is presumably due to a reduction in solid state/easily soluble alkalinity which is probably associated with dissolution of the amorphous mineral component (e.g. amorphous precursors of tricalcium aluminate and sodalite) (Grafe et al. 2011) and leaching of liberated alkalinity during the leaching period. Indeed, the nature of the amorphous mineral component in bauxite residues and its relationship with the residual alkalinity present deserves future study. The very high residual alkalinity in the mud will make revegetation a challenge because of a continual background supply of alkalinity into solution. Even 25% addition of sand to mud caused a substantial reduction in both short-term and residual alkalinity while addition of 25% mud to sand had the opposite effect.

C. Physical properties

The high microporosity (>40%) and large quantity of water held at field capacity by mud can result in surface layers becoming waterlogged during wet periods of the year (Jones and Haynes, 2011). Although sand had a much greater macroporosity than mud, addition of sand to mud only had a substantial effect on macroporosity when the mixture contained 75% sand (Table 7). Indeed, additions of small amounts of sand (e.g. 25%) tended to reduce total porosity and had no significant effect on pore size distribution. This is attributable to the ability of small mud particles to fill macropore voids between sand particles. Additions of sand to mud at 25% are common practice (Courtney and Timpson 2004; Courtney et al. 2009) but results presented here suggest they have minimal effect on total porosity and pore size distribution of the medium.

The available water holding capacity was much less for the sand than mud and the lack of available water during dry periods can limit plant growth in residue sand. The addition of 25% mud to sand (i.e 75% sand) significantly increased available water and the quantity of water held at field capacity. Nevertheless, it also increased exchangeable Na, ESP, EC and alkalinity so that whether addition of mud to sand is a viable strategy will depend on whether physical or chemical constraints are most limiting to plant growth.

D. Germination index

Prior to leaching, germination was considerably less in mud than sand and after leaching, there was still significant inhibition of germination in mud (and mixtures containing a substantial amount of mud). The limiting factors in mud are the greater ESP, inorganic C and short-term and residual acid

neutralizing capacity than sand. As already noted, a reduction in ESP can be achieved by adding gypsum followed by leaching. Indeed, although germination percentage was satisfactory (>80%) in all residues after leaching, plants are unlikely to grow satisfactorily in these materials (ESP of 20-82%). Patterns for seed germination versus subsequent growth of plants in bauxite residues are often dissimilar (Jones et al. 2012a) since longer-term physiological effects of salinity/sodicity on plant growth are not assayed in short-term germination tests.

Conclusions.

Where residue sand is the medium being used for revegetation (as is the case at the site where the residues originated), low water retention (due to the course nature of the sand) can be a limitation to revegetation. Addition of fine textured mud to the sand is a possible option. Indeed, a 25% addition of mud to sand did increase available water and water held at field capacity. It also increased CEC but had the potentially detrimental effects of causing increases in exchangeable Na, ESP and short-term and residual acid neutralizing capacity. Where mud is the revegetation medium, addition of sand to the mud has been promoted as improve aeration, drainage and root penetration. However, results showed that addition of 25% sand to mud had little effect on measured physical properties although it did reduce exchangeable Na and ESP. The nature of the residual alkalinity present in residues and its relationship with the amorphous mineral fraction deserves future study.

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Table 1 pH, EC, elemental and mineralogical composition of the materials used.

Residue	pH	EC	Total Analysis (g kg^{-1})							
			Si	Fe	Al	Ca	K	Mg	Na	P
Mud	11.0	5.65	104	191	67.1	12.5	7.3	0.6	37.2	0.7
Sand	11.3	1.35	247	158	50.4	0.8	0.9	0.04	3.3	0.1

Residue	Mineralogical composition (%)												
	Quartz	Hematite	Goethite	Maghemite	Calcite	Anatase	Rutile	Boehmite	Gibbsite	Kaolin	Illite	Sodalite	Amorphous
Mud	7.1	8.5	22.2	-	6.5	0.6	0.6	3.3	1.3	-	11.7	4.1	34.2
Sand	47.6	11.2	9.9	0.9	0.2	0.1	0.5	0.4	4.3	0.5	0.8	-	23.4

Table 2 Effect of addition of increasing proportions of residue sand to residue mud on Colwell P, pH, EC, ESP, ECEC and germination index.

Sand addition (% v/v)	Colwell P (mg P kg^{-1})		pH		EC (dS m^{-1})		ESP (%)		ECEC ($cmol_c$ kg^{-1})		Germination index (%)	
	Initial	Final	Initial	Final	initial	Final	Initial	Final	Initial	Final	Initial	Final
0	116.9g	80.6g*	11.0b	10.2a*	5.6e	1.0ef*	95d	69ef*	37.7e	15.3d*	10a	86b*
25	77.6f	57.8f*	11.0b	10.2a*	4.8d	0.94e*	93cd	62d*	29.0d	11.5c*	12a	83b*
50	48.7e	37.4e	11.0b	10.1a*	3.6c	0.61c*	90c	49c*	22.2c	8.1bc*	30b	94c*
75	19.9d	21.5d	11.0b	10.0a*	2.5b	0.39b*	85b	33b*	17.7b	5.5b*	72c	94c*
100	8.5a	9.1c	11.3b	9.9a*	1.4a	0.13a*	77a	22a*	11.7a	2.8a*	90d	120d

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 3 Effect of addition of increasing proportions of residue sand to residue mud on ammonium acetate-exchangeable cations and extractable Al before (initial) and after (final) leaching.

Sand addition (% v/v)	Exchangeable cations ($cmol_c\ kg^{-1}$)								Extractable Al ($cmol_c\ kg^{-1}$)	
	Ca		Mg		K		Na			
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
0	0.9a	0.7bc	0.79c	0.56d*	0.05a	0.02a*	36d	14d*	0.19b	0.05b*
25	1.4b	1.0a	0.55bc	0.44c*	0.04a	0.01a*	27c	10c*	0.19b	0.07bc*
50	1.8bc	1.3a	0.39b	0.36bc	0.03a	0.01a	20bc	6.4b*	0.20b	0.07bc*
75	2.4c	1.8b	0.27ab	0.23b	0.03a	0.01a	15b	3.5ab*	0.19b	0.09c*
100	2.5c	1.9b	0.18a	0.08a	0.03a	0.01a	9a	1.8a*	0.22b	0.10c*

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for that particular property.

Table 4 Effect of addition of increasing proportions of residue sand to residue mud on pH, EC, Al, extractable cations and SAR in saturated paste extracts.

Sand addition (% v/v)	pH	EC (dS m^{-1})	Saturated paste extractable cations ($mmol_c$ L^{-1})					SAR
			Ca	Mg	K	Na	Al	
0	10.2a	13.2c	0.33b	0.07a	0.32a	225b	0.02c	518b
25	10.3a	12.8c	0.31b	0.03a	0.28a	225b	0.03cd	586bc
50	10.4ab	12.2b	0.26ab	0.03a	0.27a	219b	0.04cd	604c
75	10.5ab	8.26ab	0.22a	0.02a	0.22a	175ab	0.05d	556bc
100	10.6b	5.15a	0.15a	0.01a	0.16a	117a	0.06d	512b

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

Table 5 Effect of addition of increasing proportions of residue sand to residue mud on total and organic C, DTPA-extractable micronutrients and short-term and residual acid neutralizing capacity (ANC) before (initial) and after (final) leaching.

Sand addition (% v/v)	Total C (g kg^{-1})	Organic C (g kg^{-1})	DTPA – extractable metal (mg kg^{-1})				ANC (short-term)		ANC (residual)	
			Fe	Mn	Zn	Cu	Initial	Final	Initial	Final
0	20.5g	3.7g	21.5f	0.29d	0.31a	1.01e	0.28d	0.12d*	0.26e	0.15d*
25	12.8f	2.8ef	20.7f	0.24c	0.27a	0.76d	0.19c	0.08c*	0.18d	0.10c*
50	7.4e	2.2c	17.4e	0.18b	0.25a	0.53c	0.11b	0.05b*	0.11c	0.07b*
75	3.8b	1.8b	11.4d	0.10a	0.21a	0.22b	0.06ab	0.02a*	0.08b	0.04ab*
100	2.0a	1.2a	9.21c	0.05a	0.22a	0.06a	0.04a	0.01a*	0.06a	0.02a*

Means followed by same letters within one column are not significantly different at $P \leq 0.05$.

* denotes a significant effect ($P \leq 0.05$) of measurement time (initial versus final) for ANC.

Table 6 Effect of addition of increasing proportions of residue sand to residue mud on mean ionic composition of leachates over the 14-week leaching period.

Sand addition (% v/v)	pH	EC (dS m^{-1})	Mean concentration ($mmol_c$ L^{-1})					
			Na^+	Ca^{2+}	K^+	Mg^{2+}	$Al(OH)_4^-$	$H_2PO_4^-$
0	10.3b	10.5b	132.7c	0.09a	0.2a	0.1a	0.07b	0.6c
25	10.4b	9.2b	122.3bc	0.07a	0.2a	0.2a	0.06b	0.5bc
50	10.4b	9.0b	115.3b	0.06a	0.2a	0.2a	0.08bc	0.3abc
75	10.5b	7.0ab	78.4a	0.05a	0.1a	0.01a	1.0c	0.1ab
100	10.6b	4.9a	58.1a	0.03a	0.1a	0.01a	0.6b	0.04a

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Table 7 Effect of addition of increasing proportions of residue sand to residue mud on physical properties

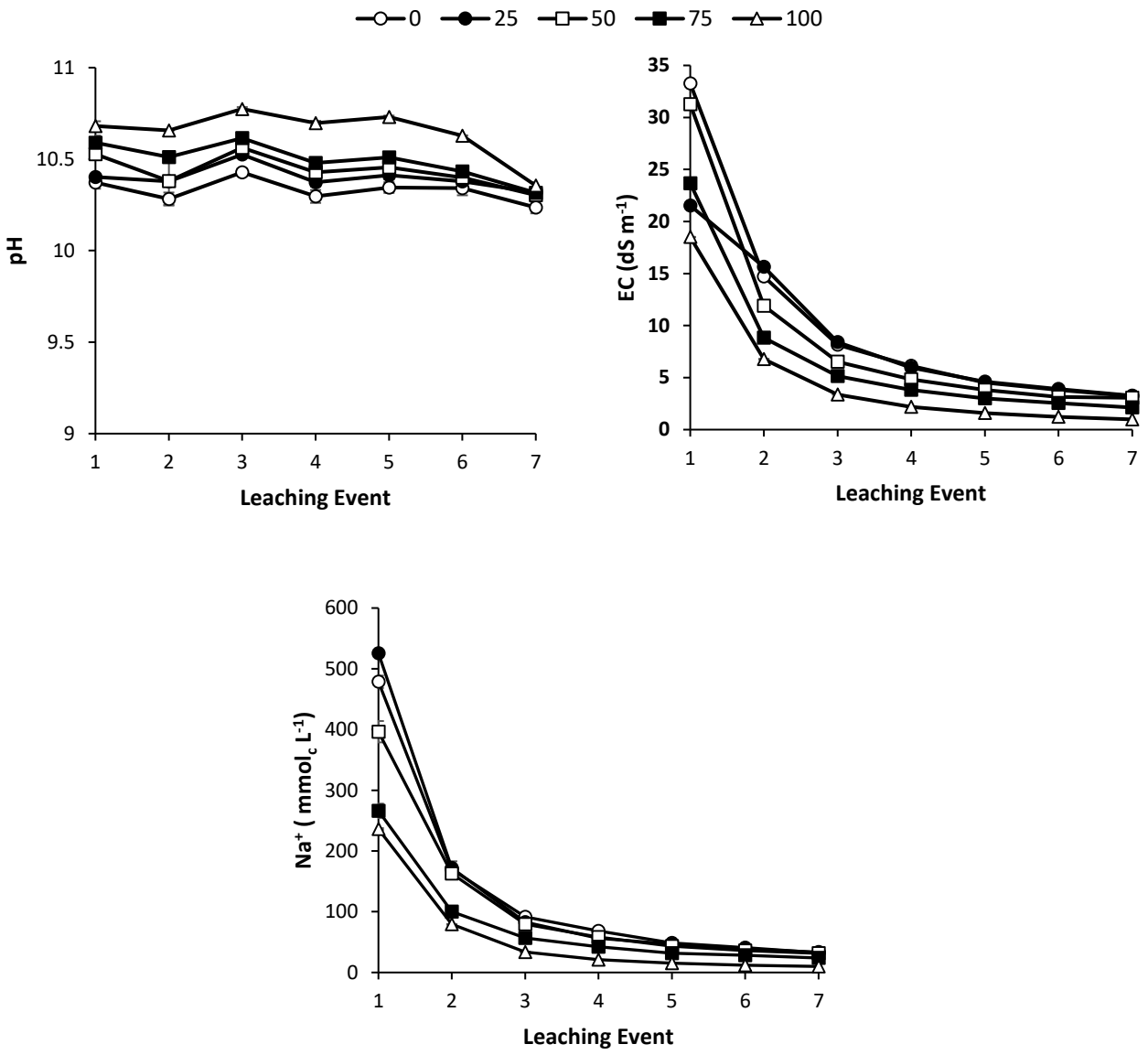
Sand addition (% v/v)	Bulk Density (mg m^{-3})	Particle Density (mg cm^{-3})	Total Porosity (m^3 m^{-3})	Pore size distribution (%)			Available Water (kg m^{-3})	Field Capacity (kg m^{-3})
				Micropores (<0.20 μm)	Mesopores (0.20-29 μm)	Macropore (>29 μm)		
0	1.31d	2.89a	0.55b	42.0d	58.0c	0a	357d	615f
25	1.52e	2.94a	0.47ab	40.7d	59.3c	0a	305c	514e
50	1.62f	2.93a	0.43a	36.1c	61.3cd	2.6b	264b	420c
75	1.71g	3.00a	0.41a	23.8b	60.5cd	15.7c	251ab	349b
100	1.78g	3.05a	0.42a	12.2a	55.0b	32.8d	230a	281a

Means followed by same letters in one column are not significant difference at $P \leq 0.05$.

Figure Captions

Fig.1 Effect of adding increasing proportions of residue sand to residue mud on the pH, EC and Na^+ concentrations in leachates during seven progressive leaching events. Standard errors of the means shown.

Fig. 1


0
25
50
75
100
pH
Leaching Event
EC (dS m-1)
Leaching Event
Na+ (mmolc L-1)
Leaching Event